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Analytical applications of the reaction of thorium with benzenephosphonic acid and its derivatives

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ANALYTICAL APPLICATIONS OF THE
REACTION OF THORIUM WITH BENZENEPHOSPHONIC
ACID AND ITS DERIVATIVES

by

Rodney James Davis

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

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Dean of Graduate College

Iowa State College
1954

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I. INTRODUCTION

A. Some Chemical Properties of Thorium

The group IVA metals are relatively poor electron acceptors and within the group the basicity increases from titanium to thorium. Williams (41) pointed out that the free energy change of chelation of a tetravalent cation is due largely to the increase in entropy, and advised the analytical chemist to choose a reagent for this group which coordinates weakly to avoid interferences from the better electron acceptors. This implies that one should choose reagents which coordinate through oxygen rather than nitrogen. In general the reagents which have been found most useful are of this type. The neutralization of charge and the independence of solubility on formation of a continuous lattice are other requisites for such reagents.

Thorium precipitates with oxalic acid as $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. However, thorium oxalate dissolves in ammonium oxalate to form ThOx_4^{-4} (36), indicating a coordination number of eight. Acetylacetone reacts with thorium, as do several β -diketones, to form compounds of the form ThA_4 (36), and with ammonia present to form $(\text{ThA}_4)_2 \cdot \text{NH}_3$ (36). The latter compound is interesting in that it appears that thorium has a coordination number greater than eight. Thorium pyrophosphate precipitates as a dihydrate (34), exhibiting a coordination number of eight for thorium. Double carbonates have been made of the form $(\text{NH}_4)_2 \text{Th}(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (36). Double sulfates are of the form $\text{M}_2\text{Th}(\text{SO}_4)_3$ and $\text{M}_4\text{Th}(\text{SO}_4)_4$ (36), indicating coordination numbers of six and eight for

thorium. Recent work by Kraus (19) suggests that the thorium ion is associated with eight molecules of water in aqueous solution. Finally, thorium oxide has been found to have the fluorite structure (38) which gives thorium a coordination number of eight.

More information of this type is available but it already seems clear that thorium usually attains its maximum coordination number of eight in these compounds in which it is coordinated with oxygen.

Zebroski (42) reported reaction constants for the complexation of thorium with phosphoric acid, as well as several other acids. The most prevalent complex ions involve a two to one ratio of phosphorus to thorium.

B. The Arsonic Acids in Analytical Chemistry

Since the first announcement of analytical applications of benzene-arsonic acid by Rice, Fogg and James (32), much information has appeared about this group of compounds. Kapulitzas (14) tested the sensitivity of a group of substituted benzenearsonic acids. Inspection of these data showed that the changes in sensitivity on substitution were only slight. The best reagent was only four times as sensitive as the poorest.

In general the arsonic acids have been found to precipitate all tetravalent cations, including U(IV), Sn(IV), Ce(IV), Ti(IV), Zr(IV), Hf(IV) and Th(IV) (37). Since U(VI), Sn(II) and Ce(III) are not precipitated, interference from these elements can usually be avoided.

Peroxide is used to prevent interference from titanium. With some difficulty zirconium can be determined in the presence of thorium by virtue of the greater solubility of the thorium salt in acid (32). Several trivalent ions tend to interfere, including Bi(III), Fe(III) and Al(III) (32, 37), but the interference can be avoided by virtue of the greater solubility of the compounds formed, in acid. Bismuth has been separated quantitatively as $\text{Bi(OH)(C}_6\text{H}_5\text{AsO}_3)$ (32).

The gravimetric determination of zirconium is completed by ignition to the oxide. The ignition must be carried out at a very high temperature or in the presence of hydrogen (32). The determination of thorium is completed by dissolving the arsonate, precipitating the thorium as the oxalate and finally igniting to the oxide (32, 37).

C. The Phosphonic Acids

Although the literature contains vast quantities of information about the organic chemistry of phosphorus, no mention is made of analytical application of phosphonic acids.

Credit should be given to Michaelis for his very early elucidation of the nature of organophosphorus compounds and to Kosolopoff and Toy as contemporary leaders in the field.

A few salient comparisons of arsenic and phosphorus are of interest here. The crystal radii of the X(V) ion in XO_3^- are 0.34 and 0.47 Å for phosphorus and arsenic, respectively (28). The corresponding electronegativities are 2.1 and 2.0 (30). The nitrogen family undergoes

an essentially regular change from a true non-metal to an almost true metal. The so-called inert pair of electrons appear in arsenic and become a dominant characteristic of bismuth (36).

The ionization constants (Table 1) of the H_3XO_4 compounds are nearly the same (36).

Table 1. Ionization Constants of Phosphoric and Arsenic Acids

K	H_3PO_4	H_3AsO_4
K_1	7.5×10^{-3}	4.8×10^{-3}
K_2	6.2×10^{-8}	1×10^{-7}
K_3	1×10^{-12}	1×10^{-13}

Jaffe', Freedman and Doak (11) and Lesfaurier and Rumph (22) determined ionization constants for a long series of substituted benzenephosphonic acids and calculated Hammett (9) reaction constants for both ionizations. Pressman and Brown (31) presented similar data for a series of arsonic acids. Tabulation of the reported constants (Table 2) for the unsubstituted acids shows that the phosphonic acids are significantly stronger acids.

Pressman and Brown (31) concluded that the most important resonance structures concerned in the ionizations did not involve a charged arsenic atom. Structures which involve 10 electrons around the central atom were suggested. Jaffe' and co-workers correlated

Table 2. The pK' Values and Hammett Reaction Constants of Benzenephosphonic and Benzenearsonic Acids

Acid	pK'_1	pK'_2	ρ_1	ρ_2
$C_6H_5PO_3H_2$	1.83	7.07	0.755	0.949
$C_6H_5AsO_3H_2$	3.47	8.48	0.953	0.874

polarizability of the central atom with reaction constants and felt that other data (10) showed that the above-described resonance structures were unlikely.

II. STATEMENT OF THE PROBLEM

The general similarity between phosphonic acids and arsonic acids indicates that the former compounds might be valuable analytical reagents just as the latter have proved to be. The increased acid strength of the phosphonic acids was expected to decrease the solubility product of the complexes formed, since one expects the anion of the acid to be the reacting species.

The aim of this work was to investigate the use of benzenephosphonic acid as an analytical reagent for thorium and to obtain some information about the fundamental chemistry involved in the reaction with thorium.

III. EXPERIMENTAL PART

A. Materials and Apparatus

1. Primary and secondary standards

1) Potassium acid phthalate. Primary standard grade lot number X 538, manufactured by Eastman Kodak Co., Rochester, New York, was used. This material was dried at 110° C. for about 2 hours before samples were taken. This material was used as a primary standard acid.

2) Disodium hydrogen phosphate. A. U. S. National Bureau of Standards standard sample 186 II was used as a phosphate standard after it was dried at 110° C.

3) Standard pH solutions. Beckman buffer powers numbers 14044 and 14049 were used according to the specifications supplied, for pH 4 and pH 9 buffers, respectively. A concentrated buffer solution, also sold by Beckman Instruments, Inc., Pasadena, California, was used to prepare a pH 7 buffer solution.

4) Standard weights. A class M set of weights which had been calibrated by the manufacturer (Wm. Ainsworth and Sons, Denver, Colorado) against a U. S. National Bureau of Standards certified secondary standard, was used to calibrate the class S weights used in this work.

2. Materials

- 1) Benzenephosphondiamide, $C_6H_5PO(NH_2)_2$. This was prepared according to Michaelis (26), m. p. 192 to 193° C. as compared to 189° C. reported.
- 2) Benzenephosphondianilide, $C_6H_5PO(C_6H_5NH)_2$. This was prepared according to Michaelis (26), m. p. 209 to 211° C. as compared to 211° C. reported.
- 3) Benzenephosphonic acid, $C_6H_5PO_3H_2$. Eastman practical grade was used. The melting point (161° C.) agreed very well with literature values (17). Potentiometric titration with standard base showed that the equivalents of base between endpoints was equal to the equivalents to the first end point. The ratio of the former to the latter was 1.003. Solutions were prepared by dissolution in deionized water and filtering. Solutions were standardized where necessary against standard alkali.
- 4) Benzenephosphoryldichloride, $C_6H_5POCl_2$. This material was obtained from the Victor Chemical Works, Chicago, Illinois. The refractive index (n_D^{25}) was 1.553 as compared to 1.558 reported (17).
- 5) Dimethylbenzenephosphonate, $C_6H_5PO(OCH_3)_2$. This material was prepared by the reaction of benzenephosphoryldichloride with methanol (18) and purified by vacuum distillation. The refractive index ($n_D^{25} = 1.5060$) compared well with that observed by workers at the Victor Chemical Works laboratory ($n_D^{25} = 1.500$) (3).

6) Phosphobenzene, $C_6H_5PO_2$. This chemical was prepared according to Michaelis (25), m. p. 100 to 103° C. as compared to 100° C. reported.

7) Thorium nitrate. Hydrated thorium nitrate obtained from the Lindsay Chemical Co., West Chicago, Illinois, was recrystallized from water. Solutions were prepared by dissolving in deionized water and filtering. Solutions were standardized by the classical oxalate method (34).

8) Karl Fisher reagent and standard water in methanol reagent. These reagents were made according to Seaman, McComos and Allen (35).

9) All other chemicals used were of reagent grade.

3. Apparatus

1) Balances. A type TCX keyboard analytical balance manufactured by Wm. Ainsworth and Sons, Inc., Denver, Colorado, was used for most weighings, in conjunction with a set of class S, rhodium-plated, bronze, two-piece weights. The class S weights were calibrated against a class M set. Some weighings were made with a five-place Gramatic balance distributed by Fisher Scientific Co., Pittsburgh, Pennsylvania. An Ainsworth type FDJ micro balance was used where six-place accuracy was necessary.

2) Conductance apparatus. A number 4866 conductivity bridge manufactured by Leeds and Northrup Co., Philadelphia, Pennsylvania, was used, with a dipping conductivity cell number 4920, also made by Leeds and Northrup.

3) Glassware. Pyrex class A pipettes, manufactured by the Corning Glass Works, Corning, New York; Exax volumetric flasks produced by Kimble Glass, Toledo, Ohio; and Normax and Ultramax burettes made by Kimble Glass and the Nalge Co., Rochester, New York, respectively, were used.

4) Filter crucibles. Sela crucibles of number 10 porosity produced by the Sela Corp. of America, Philadelphia, Pennsylvania, were used. Alundum crucibles made by the Norton Co., Worcester, Massachusetts, were used for high temperature ignitions.

5) Oscillometer. The Sargent Model V Chemical Oscillometer with cell holder type B, manufactured by Sargent and Co., Chicago, Illinois, was used.

6) pH Meters. Beckman pH meters model G and H₂, produced by Beckman Instruments Co., Inc., Pasadena, California, were used.

7) Spectrophotometer. The Cary recording spectrophotometer, a product of the Applied Physics Corp., Pasadena, California, was used.

8) Thermobalance. The automatic recording balance made by Brown et al. (2) was used. The temperature was increased in the upright muffle furnace by hand operation of a Variac and measured with a chromel-alumel couple in conjunction with a potentiometer.

9) Water determination apparatus. The azeotrope distillation apparatus of Roberts and Levin (33) was used. Automatic zeroing

Ultramax burettes were fitted by means of glass joints to the titration flask, and gravity fed from storage bottles which were protected from the atmosphere by drying tubes filled with indicating silica gel. The dead stop end-point device of McKinney and Hall (24) was used.

B. Data and Results

1. Development of precipitation procedure of thorium with benzenephosphonic acid

A series of qualitative tests determined optimum conditions for the precipitation of thorium. One hundred fifty ml. of a solution of thorium nitrate containing about 0.1 g. of thorium was used for each test. Acidity was adjusted with concentrated hydrochloric acid. In most tests the solutions were digested hot for an hour or more; therefore, the final acidity was not known exactly. Complete precipitation was ascertained by neutralization of the decanted supernatant solution with sodium hydroxide.

Tests with a 2.5 per cent solution of benzenephosphonic acid showed: 1) Precipitation was complete in solutions initially 0.4 to 1.0 N, if a ten-fold excess of reagent was used (assuming a two to one reaction of the reagent with thorium). 2) Precipitation was complete from solutions initially 1.0 N in acid, if a two-fold or greater excess of reagent was used. 3) Complete homogeneous precipitation could be effected with the customary use of urea and approximately a three-fold excess of reagent. The quality of the precipitate, however, was not improved. 4) The quality of the precipitate was bettered in the

direct precipitation, when the hot reagent solution was added slowly to a boiling sample solution. 5) In general, the quality of the precipitate varied directly with the acidity of the solution.

6) Digestion in fairly concentrated acid for 1 hour improved the character of the precipitate.

In the tests using dimethylbenzenephosphonate, the ester was added to the boiling sample solutions and the boiling was continued for 1 hour. The following observations were made: 1) A ten-fold excess of reagent precipitated thorium completely from solutions initially 1.0 N in acid, but precipitation was incomplete from solutions initially less acid. 2) A four- to ten-fold excess of reagent completely precipitated thorium from 1.0 N acid, whereas a two-fold excess was insufficient. 3) The quality of the precipitate was excellent. 4) The rate of precipitation varied directly with the acidity on the solution.

Tests made using the reagent phosphobenzene as a fresh alcohol solution showed: 1) A ten-fold excess of reagent completely precipitated thorium from 0.4 to 1.0 N acid. 2) From 1.0 N acid, precipitation was complete with a ten-fold excess of reagent but not with an eight-fold excess or less. 3) The quality of the precipitate was no better, using this reagent, than that of the precipitate effected with the free acid reagent. 4) Precipitation occurred immediately upon addition of the reagent.

Tests with benzenephosphondiamide showed that fresh solutions of this reagent in glacial acetic acid precipitated thorium incompletely

from 1.0 N hydrochloric acid, if boiled for an hour. Considerable reagent precipitated upon adding the acetic acid solution to the aqueous sample solution.

Benzenephosphondianilide was also prepared in glacial acetic acid, but the reagent precipitated upon being added to the aqueous thorium solution. After boiling for an hour, it was apparent that very little or none of the thorium was precipitated.

With these tests as a basis, further testing was made of the use of the free benzenephosphonic acid, phosphobenzene and dimethylbenzenephosphonate. The procedure followed was: 1) A thorium nitrate sample containing 0.02 to 0.2 g. of thorium was placed in a 600-ml. beaker. 2) A 100- to 150-ml. portion of 1:3 hydrochloric acid solution was added. 3) The solution was heated to boiling. 4) The reagent was added. Either 0.60 g. of phosphobenzene, dissolved in alcohol, 1.2 ml. of dimethylbenzenephosphonate, specific gravity 1.195, or 50 ml. of 2.5 per cent benzenephosphonic acid solution were used in each case to provide at least a five-fold excess of reagent. 5) The solution was then boiled 1 hour. 6) In those cases where phosphobenzene or dimethylbenzenephosphonate were used, 10 ml. of 2.5 per cent benzenephosphonic acid were added at this point. 7) The solution was diluted to 300 to 400 ml. 8) The pH was adjusted and the precipitate was allowed to settle for several hours. 9) Sela filter crucibles were used to collect the precipitate which was then ignited and weighed. 10) The filtrate was tested for thorium with ammonia.

At this stage in the experiments there were three important variables in the precipitating procedure to be determined: 1) The pH range of complete precipitation. 2) The amount of excess reagent for complete precipitation. 3) The drying or ignition temperature. The last variable was estimated by the preliminary thermogravimetric curves, subsequently described, which showed the best plateau at 100° to 240° C. To precisely determine the maximum drying temperature, a series of precipitations were made according to the above procedure. Fifty ml. of 2.5 per cent benzenephosphonic acid, about a nine-fold excess, was used as the reagent and the pH was adjusted as shown in Table 3. Each precipitate was dried for 3 hours at 110°, 120°, 130°, 140°, 150°, 160°, 170°, 180°, and 190° C. The results are shown in Table 3. The filtrates were all tested for thorium by neutralization and all the filtrates remained clear even after several days, showing that precipitation was complete.

It was of interest next to establish the low extreme of the pH range. Table 3 shows that the low extreme is less than 0.5. To gain this information, two sets of precipitations were carried out, one at pH 0.5, a second at pH 0.1. The precipitates were dried at 120° C. to constant weight. The pertinent data are in Table 4. All of the filtrates were neutralized with ammonia. Those filtrates from the pH 0.1 series became cloudy; those from the pH 0.5 series remained clear.

The final thing to determine was the necessary amount of excess reagent. Tables 3 and 4 show that a nine-fold excess is adequate.

Table 3. Effect of Drying Temperature on Thorium Benzenephosphonate Precip

Sample no.	pH	Sample wt. (g. Th)	Weight of precipitate dried at:							
			110° C.	120° C.	130° C.	140° C.	150° C.	160° C.	170° C.	180° C.
1	0.5	0.06651	0.1767	0.1745	0.1720	0.1714	0.1712	0.1711	0.1711	0.171
2	0.5	0.08868	0.2292	0.2280	0.2273	0.2271	0.2268	0.2268	0.2267	0.226
3	0.5	0.11085	0.2920	0.2891	0.2866	0.2856	0.2856	0.2856	0.2855	0.285
4	1.0	0.06651	0.1768	0.1743	0.1719	0.1717	0.1704	0.1705	0.1704	0.170
5	1.0	0.08868	0.2272	0.2261	0.2256	0.2254	0.2252	0.2252	0.2251	0.225
6	1.0	0.11085	0.2878	0.2857	0.2841	0.2838	0.2836	0.2837	0.2835	0.283
7	1.5	0.06651	0.1753	0.1732	0.1710	0.1700	0.1698	0.1698	0.1699	0.169
8	1.5	0.08868	0.2266	0.2265	0.2262	0.2260	0.2259	0.2260	0.2260	0.225
9	1.5	0.11085	0.2854	0.2843	0.2832	0.2829	0.2828	0.2829	0.2828	0.282
10	2.0	0.06651	0.1751	0.1734	0.1717	0.1704	0.1703	0.1705	0.1704	0.170
11	2.0	0.08868	0.2309	0.2300	0.2285	0.2279	0.2278	0.2282	0.2280	0.228
12	2.0	0.11085	0.2920	0.2893	0.2867	0.2857	0.2854	*	*	*
13	2.5	0.06651	0.1692	0.1691	0.1689	0.1688	0.1687	0.1690	0.1689	0.169
14	2.5	0.08868	0.2290	0.2273	0.2261	0.2259	0.2258	0.2260	0.2259	0.226
15	2.5	0.11085	0.2902	0.2884	0.2869	0.2863	0.2859	0.2860	0.2858	0.285
16	3.0	0.06651	0.1724	0.1722	0.1718	0.1717	0.1715	0.1717	0.1715	0.171
17	3.0	0.08868	0.2281	0.2279	0.2276	0.2275	0.2274	0.2275	0.2274	0.227
18	3.0	0.11085	0.2903	0.2878	0.2857	0.2852	0.2851	0.2852	0.2849	0.285
19	3.5	0.06651	0.1749	0.1734	0.1723	0.1721	0.1719	0.1720	0.1719	0.172
20	3.5	0.08868	0.2286	0.2283	0.2282	0.2280	0.2279	0.2280	0.2279	0.227
21	3.5	0.11085	0.2861	0.2858	0.2856	0.2855	0.2853	0.2854	0.2853	0.285

*Sample accidentally spilled.

Effect of Drying Temperature on Thorium Benzenephosphonate Precipitate Weights

t.	Weight of precipitate dried at:									Weight lost from 140°-180° C.
	110° C.	120° C.	130° C.	140° C.	150° C.	160° C.	170° C.	180° C.	190° C.	
	0.1767	0.1745	0.1720	0.1714	0.1712	0.1711	0.1711	0.1710	*	0.0004
	0.2292	0.2280	0.2273	0.2271	0.2268	0.2268	0.2267	0.2267	0.2260	0.0004
	0.2920	0.2891	0.2866	0.2856	0.2856	0.2856	0.2855	0.2852	0.2846	0.0004
	0.1768	0.1743	0.1719	0.1717	0.1704	0.1705	0.1704	0.1705	0.1702	0.0002
	0.2272	0.2261	0.2256	0.2254	0.2252	0.2252	0.2251	0.2251	0.2245	0.0003
	0.2878	0.2857	0.2841	0.2838	0.2836	0.2837	0.2835	0.2832	0.2823	0.0006
	0.1753	0.1732	0.1710	0.1700	0.1698	0.1698	0.1699	0.1697	0.1695	0.0003
	0.2266	0.2265	0.2262	0.2260	0.2259	0.2260	0.2260	0.2259	0.2258	0.0001
	0.2854	0.2843	0.2832	0.2829	0.2828	0.2829	0.2828	0.2829	0.2825	0.0000
	0.1751	0.1734	0.1717	0.1704	0.1703	0.1705	0.1704	0.1705	0.1703	0.0001
	0.2309	0.2300	0.2285	0.2279	0.2278	0.2282	0.2280	0.2280	0.2270	0.0001
	0.2920	0.2893	0.2867	0.2857	0.2854	*	*	*	*	*
	0.1692	0.1691	0.1689	0.1688	0.1687	0.1690	0.1689	0.1691	0.1689	0.0003
	0.2290	0.2273	0.2261	0.2259	0.2258	0.2260	0.2259	0.2260	0.2259	0.0001
	0.2902	0.2884	0.2869	0.2863	0.2859	0.2860	0.2858	0.2857	0.2855	0.0006
	0.1724	0.1722	0.1718	0.1717	0.1715	0.1717	0.1715	0.1715	0.1715	0.0002
	0.2281	0.2279	0.2276	0.2275	0.2274	0.2275	0.2274	0.2273	0.2273	0.0002
	0.2903	0.2878	0.2857	0.2852	0.2851	0.2852	0.2849	0.2850	0.2848	0.0002
	0.1749	0.1734	0.1723	0.1721	0.1719	0.1720	0.1719	0.1720	0.1718	0.0001
	0.2286	0.2283	0.2282	0.2280	0.2279	0.2280	0.2279	0.2279	0.2278	0.0001
	0.2861	0.2858	0.2856	0.2855	0.2853	0.2854	0.2853	0.2853	0.2852	0.0002

ally spilled.

Table 4. Effect of pH on Thorium Benzenephosphonate Precipitate Weights

(Dried at 120° C.)

Sample no.	Sample wt. (g. Th)	Wt. ppt. (g.)	Wt. ppt. per 232.12 g. Th
pH = 0.1			
1	0.04434	0.1128	588.1
2	0.04434	0.1127	587.6
3	0.04434	0.1139	593.8
4	0.06651	0.1687	586.3
5	0.06651	0.1715	596.1
6	0.06651	0.1700	590.9
7	0.08868	0.2265	590.4
8	0.08868	0.2274	592.8
9	0.08868	0.2241	584.2
10	0.08868	0.2257	588.3
11	0.11085	0.2834	591.0
12	0.11085	0.2853	595.0
13	0.11085	0.2832	590.7
14	0.11085	0.2831	590.4
			Av. 590.4
pH = 0.5			
15	0.04434	0.1152	603.1
16	0.04434	0.1148	601.0
17	0.04434	0.1142	597.8
18	0.06651	0.1700	591.7
19	0.06651	0.1759	612.2
20	0.06651	0.1713	596.2
21	0.08868	0.2276	596.4
22	0.08868	0.2330	610.5
23	0.08868	0.2307	604.5
24	0.08868	0.2291	600.3
25	0.11085	0.2859	598.7
26	0.11085	0.2856	598.0
27	0.11085	0.2881	603.3
28	0.11085	0.2851	597.0
			Av. 600.8

Table 4 (Continued)

Sample no.	Sample wt. (g. Th)	Wt. ppt. (g.)	Wt. ppt. per 232.12 g. Th
pH = 1.0			
29	0.06651	0.1743	608.5
30	0.08868	0.2261	591.9
31	0.11085	0.2857	598.3
			Av. 599.6
pH = 1.5			
32	0.06651	0.1732	604.6
33	0.08868	0.2265	593.0
34	0.11085	0.2843	595.3
			Av. 597.6
pH = 2.0			
35	0.06651	0.1734	605.3
36	0.08868	0.2300	602.1
37	0.11085	0.2893	605.8
			Av. 604.4
pH = 2.5			
38	0.06651	0.1691	590.3
39	0.08868	0.2273	595.1
40	0.11085	0.2884	603.9
			Av. 596.4
pH = 3.0			
41	0.06651	0.1722	601.2
42	0.08868	0.2279	596.6
43	0.11085	0.2878	602.7
			Av. 600.2

Table 4 (Continued)

Sample no.	Sample wt. (g. Th)	Wt. ppt. (g.)	Wt. ppt. per 232.12 g. Th
pH = 3.5			
44	0.06651	0.1734	605.3
45	0.08868	0.2283	597.7
46	0.11085	0.2858	598.5
			Av. 600.5

Table 5 shows the effect of a 1.7- to 13.8-fold excess of reagent. The filtrates from sample numbers 4, 5, 6, 7, 8, 9, 12, 13 and 14 in Table 5 were tested for thorium by neutralizing with ammonia. Filtrate number 12 showed a slight opalescence; numbers 13 and 14 were definitely cloudy.

The precipitating procedure used in the remainder of the work (with the exception of the thermogravimetric work), was that outlined in the early part of the section, with the following added stipulations:

- 1) Benzenephosphonic acid was used exclusively as the reagent. 2) A five-fold or greater excess of reagent was used. 3) The pH was adjusted, after the bulk of the precipitation had occurred, to 0.5 to 1.0.
- 4) The precipitates were dried to constant weight at 150° C.

2. Thermogravimetric study of thorium benzenephosphonate

The thermogravimetric data were obtained in two distinct experiments. In the first experiment, the automatic recording balance of

Table 5. Effect of Varying Excess Reagent on
Thorium Benzenephosphonate Precipitate Weights

(Precipitated at pH 0.5; dried at 120° C.)

Sample no.	Sample wt. (g. Th)	<u>Amount reagent used</u> (g.) (Times excess)		Wt. ppt. dried 140° C.	Wt. per 232.12 g. Th
1	0.0665	1.25	13.8	0.1714	598.7
2	0.0887	1.25	10.3	0.2271	594.3
3	0.1060	1.25	8.7	0.2735	598.9
4	0.1060	1.25	8.7	0.2734	598.7
5	0.1060	1.25	8.7	0.2741	600.2
6	0.1108	1.25	8.3	0.2856	598.3
7	0.1108	0.90	5.9	0.2823	591.4
8	0.1108	0.90	5.9	0.2832	593.3
9	0.1108	0.70	4.6	0.2838	594.5
10	0.2120	1.25	4.3	0.5484	600.4
11	0.2120	1.25	4.2	0.5499	602.1
12	0.1108	0.50	3.3	0.2832	593.3
13	0.1108	0.50	3.3	0.2788	584.1
14	0.1108	0.25	1.7	0.2799	586.4

Brown et al. (2) was used. This experiment was made as a part of the work designed to set up the specifications for quantitative precipitation of thorium benzenephosphonate. The samples used were not results of quantitative precipitations. The weights of thorium in the initial precipitates were not known; therefore, only transition temperature ranges and relative weights of the compounds formed could be observed.

In the experiment, samples of thorium benzenephosphonate, dried to constant weight at 120° C., were weighed into a size 000 Coors crucible. The crucible was suspended in a quartz ring, on the end of a quartz rod, in the center portion of a vertical muffle furnace. Of course, the quartz rod was suspended from the left end of the balance beam. The thermocouple was mounted 5 to 10 mm. beneath the crucible. The sensitivity of the balance was adjusted to about 1.35 scale divisions per milligram. The sensitivity was observed by dropping a series of 10-mg. weights on the balance pan and observing the deflection before and after each run. A series of 22 such determinations showed an average deviation of ± 0.5 mg. The rate of increase in temperature was 6° C. per minute or from 100 to 1000° C. in 2 1/2 hours as recommended by Duval (5). The accuracy in temperature was limited by the ability of the operator to properly adjust the controlling Variac. The error involved was of the order of $\pm 10^\circ$ C. After each run the samples were weighed on an analytical balance, and the final sample weight determined as a check on the performance of the automatic balance.

The data are presented in Table 6. The column headed "Fraction original wt." presents the weight data in such a manner that succeeding results may be directly compared. A reproduction of the thermogravimetric curves is given in Fig. 1.

The second experiment was designed to alleviate the shortcomings of the first. Samples of known thorium content, i.e., results of quantitative precipitations, were used. Quantitative precipitation was insured by testing filtrates by neutralization. The dryings and ignitions were carried out in a drying oven at 120° and 250° C. and in a muffle furnace at 500°, 900°, 1000° and 1200° C. (temperatures corresponding to the beginnings of the plateaus observed in the first experiments) to constant weight. It was felt that more accurate weights could be observed by the latter method of ignition, rather than by use of the automatic balance. It was decided, furthermore, to restrict this study to the use of benzenephosphonic acid as precipitating reagent, since the use of phosphobenzene presented no advantages and the dimethyl ester appeared to precipitate a non-homogeneous material (see p. 66). The drying temperatures were measured with a mercury thermometer and were accurate to $\pm 2^\circ$ C. The temperature of the muffle furnace was measured with a calibrated microvoltmeter in conjunction with a chromel-alumel thermocouple. The meter was checked with a thermocouple-potentiometer combination and found to be accurate to $\pm 10^\circ$ C. The high temperature (1200° C.) ignitions were made on weighed quantities of thorium benzenephosphonate, previously dried at 150° C., in tared

Table 6. Preliminary Thermogravimetric Data

Precipitating reagent	Temp. ranges of stability ($^{\circ}$ C.)	Wt. ppt. (g.)	Fraction original wt.
Benzene-phosphonic acid	100-250	0.254	1.000
	300-400	0.247	0.972
	650-790	0.189	0.744
	1000-	0.182	0.717
	Final wt.	0.181	
Benzene-phosphonic acid*	100-210	0.237	1.000
	270-490	0.227	0.958
	640-850	0.185	0.781
	1000-	0.171	0.722
	Final wt.	0.171	
Phospho-benzene*	100-240	0.253	1.000
	300-440	0.245	0.968
	610-820	0.200	0.791
	1000-	0.183	0.723
	Final wt.	0.181	
Phospho-benzene	100-240	0.248	1.000
	290-430	0.241	0.972
	600-870	0.191	0.770
	1000-	0.176	0.710
	Final wt.	0.178	
Phospho-benzene	100-230	0.252	1.000
	270-460	0.245	0.972
	600-850	0.195	0.774
	1000-	0.182	0.722
	Final wt.	0.182	

*These runs were recorded in Fig. 1.

Table 6 (Continued)

Precipitating reagent	Temp. ranges of stability (* C.)	Wt. ppt. (g.)	Fraction original wt.
Dimethyl-benzene-phosphonate*	100-280	0.251	1.000
	600-820	0.159	0.633
	970-1000	0.152	0.610
	Final wt.	0.158	
Dimethyl-benzene-phosphonate	100-280	0.345	1.000
	650-870	0.211	0.612
	990-1000	0.195	0.565
	Final wt.	0.194	

*These runs were recorded in Fig. 1.

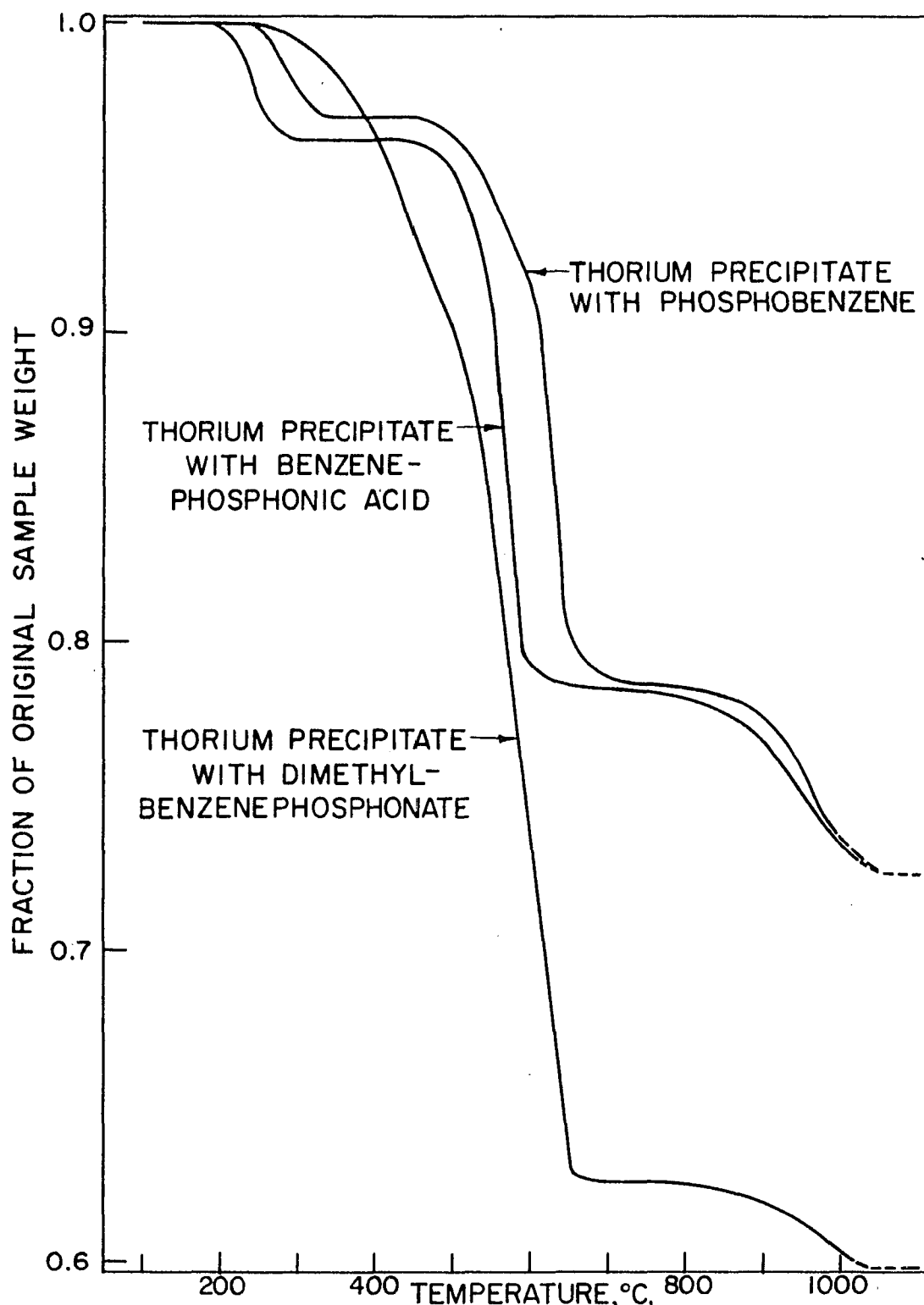


FIG. 1 THERMOGRAVIMETRIC CURVES

alundum crucibles. The ignitions were carried out in a high temperature muffle furnace. Table 7 summarizes the final thermogravimetric data.

3. Analyses of thorium benzenephosphonate

a. Thorium. All of the gravimetric results in which quantitative precipitation of thorium was proved by testing the filtrates with ammonia, may be construed as thorium analyses. These results are included in Table 7. Similar data in Table 11 also may be termed thorium analyses, since the precipitating procedure used had been proved to be quantitative. The average result from Table 7 was 38.60 ± 0.28 per cent thorium; from Table 11, 38.76 ± 0.14 per cent thorium. The latter value is probably more accurate, since the preferred drying temperature of 150° C. was used.

b. Water. Following the recommendation of Mitchell (27), a search for a suitable nonaqueous solvent for thorium benzenephosphonate was made. It was found that dioxane, alcohol, methanol, acetone, pyridine, nitrobenzene, mesityl oxide, benzene and dimethylformamide would not dissolve thorium benzenephosphonate in appreciable quantities.

A titration of a slurry in methanol, even after violent mixing for several hours, showed no water to be released. The dead-stop end point apparatus did not function well in the slurry and the visual end point was extremely difficult to see.

Next, the azeotrope distillation method of Roberts and Levin (33) was tried. This technique involved distilling benzene in the presence

Table 7. Final Thermogravimetric Data
and Thorium Determinations

Sample no.	Wt. Th used (g.)	Wt. ppt. (g.)	% Th	Wt. ppt. per 232.12 g. Th (g.)	Dev. from av. p./1000
Dried at 120° C.					
1	0.04434	0.1151	38.52	602.5	2.2
2	0.04434	0.1148	38.62	601.0	0.3
3	0.04434	0.1142	38.83	595.4	9.6
4	0.06651	0.1703	39.05	594.4	11.3
5	0.06651	0.1762	37.75	614.9	22.8
6	0.06651	0.1716	38.76	598.9	3.8
7	0.08868	0.2279	38.91	596.5	7.8
8	0.08868	0.2331	38.04	610.1	14.8
9	0.08868	0.2309	38.41	604.4	5.3
10	0.08868	0.2293	38.67	600.2	1.7
11	0.11085	0.2861	38.75	599.1	3.2
12	0.11085	0.2858	38.78	598.5	4.5
13	0.11085	0.2883	38.45	603.7	4.2
14	0.11085	0.2852	38.87	597.2	6.6
		Av. 38.60		601.2	7.0
Dried at 250° C.					
2	0.04434	0.1126	39.38	587.0	14.7
5	0.06651	0.1650	40.31	573.5	8.7
8	0.08868	0.2207	40.18	575.3	5.5
12	0.11085	0.2773	39.97	578.3	0.3
		Av. 39.96		578.5	7.3
Ignited at 500° C.					
6	0.06651	0.1325	50.20	460.5	1.7
9	0.08868	0.1775	49.96	462.7	3.0
10	0.08868	0.1748	50.73	455.7	12.1
13	0.11085	0.2236	49.58	466.3	10.8
		Av. 50.12		461.3	6.9

Table 7. (Continued)

Sample no.	Wt. Th used (g.)	Wt. ppt. (g.)	% Th	Wt. ppt. per 232.12 g. Th (g.)	Dev. from av. p./1000
Ignited at 900° C.					
2	0.04434	0.0815	54.50	424.9	0.9
5	0.06651	0.1234	53.90	428.3	8.5
8	0.08868	0.1643	53.97	428.3	7.1
12	0.11085	0.2025	54.74	422.3	7.1
14	0.11085	0.2024	54.77	422.1	7.5
		Av. 54.36		425.3	6.2
Ignited at 1000° C.					
2	0.04434	0.0815	54.40	424.9	0.5
5	0.06651	0.1233	53.94	428.5	8.0
6	0.06651	0.1216	54.70	422.6	5.9
8	0.08868	0.1642	54.01	428.0	6.8
9	0.08868	0.1633	54.30	425.7	1.4
10	0.08868	0.1622	54.67	422.8	5.4
12	0.11085	0.2024	54.77	422.1	7.1
13	0.11085	0.2052	54.02	427.9	6.6
14	0.11085	0.2023	54.79	421.9	7.5
		Av. 54.40		425.1	5.6
Ignited at 1200° C.					
15	0.2084*	0.3807	54.74	423.9	1.2
16	0.4260*	0.7803	54.59	425.2	2.8
17	0.2317*	0.4240	54.65	424.7	0.7
		Av. 54.66		424.4	1.9

*Samples weighed as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$; dried at 150° C. Weight of thorium calculated.

of the sample into a titration vessel. The water is expected to be leached from the sample and distilled with the benzene as an azeotrope.

In this experiment, it was found that even when the utmost precautions were taken, portions of benzene distillate, when no sample was present, required a significant volume of Karl Fisher reagent. This effect was more apparent than real and mainly due to the strength of the reagent (0.538 mg. water per ml.). The amount of water titrated in a series of 100-ml. portions of distillate usually was less than 1 mg. and was constant within ± 0.05 mg. for any given series.

The following procedure was finally developed. The distillation flask was filled with about 750 ml. of redistilled benzene. About half of this was distilled into the titration vessel, and discarded. The sample (dried at 150° C.) was added, the liquid in the titration vessel was titrated to the end point and the distillation was continued. Each 100-ml. portion of distillate was titrated and discarded as the distillation proceeded, until a very small amount of benzene remained in the flask. The end points were approached each time with the standard water solution since this method has been recommended (27).

In each determination it was found that very nearly the same quantity of reagent was required for the second 100-ml. portion of distillate as for the third and fourth portions, indicating that all of the water that could be removed from the sample was distilled over in the first 100-ml. portion. The excess reagent was necessary to

titrate small amounts of water that continued to distill over as long as the distillation proceeded.

It was also found, on going through the procedure without a sample, that similar amounts of reagent were required for the first 100-ml. portion as for the succeeding ones. Following the reasoning outlined above, this indicated that no water was involved in excess of that small amount that was a linear function of the distillate collected.

The results are shown in Table 8. Included also in Table 8 are results from similar experiments in which xylene was substituted for benzene with the idea of realizing some benefit from the higher boiling point of the water azeotrope.

The Karl Fisher reagent was standardized by titrations with weighed samples of water. The strength of the reagent was 0.538 mg. of water per milliliter. The samples used were dried at 150° C.

c. Phosphorus. Phosphorus was determined in thorium benzene-phosphonate samples which had been ignited to constant weight at 1200° C. The analyses were performed according to the following procedure. Samples were weighed into tall (about 4-inch) platinum crucibles. About 1 g. of potassium bifluoride was added and the mixture was heated until all of the material was fused. This quantitatively converted thorium as thorium fluoride. The solid material was next taken up in 48 per cent hydrofluoric acid solution. Slight heating was necessary to dissolve the soluble part and reduce the thorium fluoride to a powder. The solution

Table 8. Water Determination in Thorium Benzenephosphonate

Sample no.	Sample wt. (g.)	Ml. K. F. reagent per 100-ml. distillate				Blank cor- rec- tion	Net K. F. reagent	% H ₂ O
		1	2	3	4			
Benzene as azeotrope former								
1	0.0454	3.25	2.03	2.07	2.20	2.10	1.15	1.4
2	0.0521	1.08	0.67	0.83		0.75	0.33	0.4
3	0.1267	2.90	1.45	1.44	1.44	1.44	1.46	0.6
4	0.0000	2.85	2.82	2.83		2.83	0.02	0.0
Xylene as azeotrope former								
5	0.0534	2.33	2.13	2.16		2.15	0.18	0.0

containing phosphate was separated from the precipitate by centrifugation in lusteroid centrifuge tubes. The precipitate was washed three times with approximately 1:1 hydrofluoric acid solution by decantation, and the washings were added to the phosphate solution. The acid fluoride solution was put in a platinum dish, where 20 ml. of concentrated perchloric acid was added. This mixture was evaporated almost to dryness with an infrared evaporator. The evaporation removed fluoride from the solution, leaving potassium perchlorate and potassium phosphate. This material was dissolved in 300 ml. of deionized water. The large volume was necessary to dissolve the potassium perchlorate.

Finally, this solution was titrated with standard base, using a Beckman Model H₂ pH meter, to measure the pH. The end points were detected by the method of Gran (7). The number of equivalents of phosphate were represented by the difference in the two end points. Any perchloric acid or hydrofluoric acid which remained after evaporation was titrated with the first hydrogen on the phosphoric acid. The titration of the second phosphate proton occurred without interference. The method was proved by analysis of primary standard disodium hydrogen phosphate. The results of all the phosphate analyses are given in Table 9. The standard base was prepared by mixing a nearly saturated solution of sodium hydroxide, which had been centrifuged, with freshly deionized water. The base was standardized by titration with primary standard potassium acid phthalate, using the pH meter to detect the end point.

Table 9. Phosphorus Determination in Ignited
Thorium Benzenephosphonate

Sample no.	Sample wt. (g.)	Ml. base (0.1907 N)	% P	Dev. from av. p./100
1	0.2128	5.35	14.9	2
2	0.1534	3.81	14.7	1
3	0.2274	5.69	14.8	1
4	0.1664	4.12	14.6	0
5	0.2014	4.84	14.2	3
6	0.1487	3.62	14.4	1
7	0.3554	8.64	14.4	1
8	0.2998	7.39	14.6	0
9	0.4274	10.41	14.4	1
		Av.	14.6	1
Na_2HPO_4	0.1004	3.72	21.9	0
Na_2HPO_4	0.1387	5.17	22.0	1
Na_2HPO_4	0.1983	7.10	21.6	1
		Av.	21.8	1
Calculated 21.8				

d. Benzenephosphonate. Thorium benzenephosphonate, dried at 150°C. , was analyzed for benzenephosphonate by virtue of its spectra in the ultraviolet. Concentrated hydrochloric acid was found to be a good solvent, since it dissolved the sample readily and does not absorb appreciably at the wavelength used ($264.6\text{ m}\mu$). Thorium benzenephosphonate solutions were made up by mixing appropriate volumes of a standard thorium and standard benzenephosphonic acid solution to obtain a thorium to benzenephosphonic acid ratio of 1:2 and dilution with concentrated hydrochloric acid in a volumetric flask. Sample solutions were prepared by dissolving weighed samples, dried at 150°C. , in concentrated hydrochloric acid and diluting to volume in a 200-ml. volumetric flask.

The standard thorium solution was made by dissolving 0.0774 g. of thorium metal in concentrated hydrochloric acid solution and diluting with the concentrated acid to 200 ml. in a volumetric flask. The molarity of the thorium solution was 0.00167 and this solution was found not to absorb at $264.6\text{ m}\mu$. The standard benzenephosphonic acid solution (0.1748 M) was an aqueous solution which had been standardized with standard base. The data from this experiment are in Table 10.

The synthetic thorium benzenephosphonate solutions were used to set up a calibration curve for the determination of benzenephosphonate. The analytical results which are in Table 10 were used to make this curve.

Table 10. Benzenephosphonate Determination in
Thorium Benzenephosphonate

(b = 1.003 cm.; λ = 264.6 m μ)

Sample no.	Sample wt. (g.)	A	$M_{C_6H_5PO_3}^-$ $\times 10^3$	% $C_6H_5PO_3^-$	Dev. from av. p./100
Calibration data					
1		2.744	2.80		
2		2.064	2.10		
3		1.390	1.40		
4		0.674	0.70		
Analyses					
5	0.1094	1.844	1.85	52.8	1
6	0.0991	1.651	1.66	52.4	0
7	0.0862	1.439	1.45	52.4	0
8	0.0725	1.196	1.21	52.1	1
			Av.	52.4	1

4. Gravimetric determination of thorium with benzenephosphonic acid

a. Analyses. The determinations of thorium in thorium nitrate solution, tabulated in Table 11 were performed according to the following procedure: 1) One- to 5-ml. portions of a standard thorium nitrate solution containing 0.044 to 0.11 g. of thorium were transferred to covered 600-ml. beakers. 2) About 150 ml. of 1:3 concentrated hydrochloric acid solution were added and the solutions were heated to nearly boiling. 3) Fifty ml. of a 2.5 per cent solution of benzenephosphonic acid were added. 4) The solutions were boiled for about 1 hour. 5) The beakers were removed from the hot plate and diluted with distilled water to about 500 ml. 6) The pH was adjusted with concentrated ammonia to 0.5 to 1.0. 7) The solutions were allowed to settle, usually overnight. 8) The precipitates were filtered with coarse Sela filter crucibles and washed at least six times with hydrochloric acid of pH 0.5 to 1.0. 9) The precipitates were dried at 150° C. to constant weight. 10) The calculations were based on the precipitate's being thorium benzenephosphonate 3-hydrate, $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$, or having a molecular weight of 598.3.

The precision of the method was estimated. Values for the average, standard and probable deviation have been calculated below. Formulae for these quantities were obtained from the Kolthoff and Sandell (15) text.

$$\begin{array}{l} \text{Average deviation of a} \\ \text{single determination} \end{array} = \frac{\sum |d|}{n} = \frac{81.3}{22} = 3.7 \text{ p./1000} \quad (1)$$

Table 11. Gravimetric Determination of Thorium
 as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$

Sample no.	Wt. Th taken	Wt. ppt.	Wt. Th found	Dev. p./1000
1	0.06651	0.1712	0.06642	1.3
2	0.08868	0.2268	0.08799	7.3
3	0.11085	0.2856	0.11080	0.4
4	0.06651	0.1704	0.06612	5.9
5	0.11085	0.2836	0.11003	7.4
6	0.04434	0.1154	0.04477	9.7
7	0.04434	0.1151	0.04465	7.0
8	0.04434	0.1142	0.04431	0.7
9	0.06651	0.1703	0.06607	6.6
10	0.06651	0.1716	0.06657	0.9
11	0.08868	0.2279	0.08842	2.9
12	0.08868	0.2309	0.08858	1.1
13	0.08868	0.2293	0.08896	3.1
14	0.11085	0.2861	0.11099	1.3
15	0.11085	0.2858	0.11088	0.3
16	0.11085	0.2883	0.11185	9.1
17	0.11085	0.2852	0.11065	1.8
18	0.1060	0.2735	0.1061	0.9
19	0.1060	0.2734	0.1061	0.9
20	0.2120	0.5484	0.2128	3.8
21	0.2120	0.5498	0.2133	6.1
22	0.1060	0.2742	0.1064	2.8
Av. dev.				3.7

$$\text{Standard deviation of } a \text{ single determination} = \sqrt{\frac{\sum d^2}{n}} = \frac{500.8}{22} = 4.8 \text{ p./1000} \quad (2)$$

$$\text{Probable deviation of } a \text{ single determination} = 0.67 \sqrt{\frac{\sum d^2}{n}} = 3.2 \text{ p./1000} \quad (3)$$

The accuracy of the method was estimated by a calculation of the apparent average constant error (15) given below.

$$\text{Apparent av. constant error} = \frac{\sum d}{n} = \frac{12.7}{22} = 0.6 \quad (4)$$

Since the average constant error is less than 1/2.5 times the average deviation from the average (15), a constant error in the method cannot be assumed.

b. Interferences. Nitrate, chloride, perchlorate and sulfate solutions of 30 cations were tested for interference in the gravimetric method outlined in detail previously. The amount of interfering ion used varied from twice to one fourth the molar quantity of thorium used. These data are summarized in Table 12.

5. Titrimetric determination of thorium with benzenephosphonic acid

a. Conductimetric. The simple representation of the reaction involved in the precipitation of thorium benzenephosphonate is as follows:



Although the above equation ignores the hydrolysis of the thorium ion and ionization of the reagent acid, it is reasonable to expect a

Table 12. Interference Study of the Gravimetric Determination of Thorium as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$

Interfering substance	Interfering cation moles/mole Th	Wt. Th taken (g.)	Wt. Th found (g.)	Precision p./1000	Accuracy p./1000
NaCl	2	0.1060	0.1066	1	6
KCl	2	0.1060	0.1062	2	2
AgNO ₃	2	0.1060	0.1087	2	27
Tl ₂ SO ₄	2	0.1060	0.1153	100	93
BeCl ₂	1	0.1060	0.1067	3	7
Mg(ClO ₄) ₂	1	0.1060	0.1064	1	4
CaCl ₂	1	0.2120	0.2127	2	3
SrCl ₂	1	0.2120	0.2143	1	11
BaCl ₂	1	0.1060	0.1060	2	0
CuSO ₄	1	0.2120	0.2136	0	8
ZnCl ₂	1	0.2120	0.2134	1	7
CdCl ₂	1	0.2120	0.2140	1	5
Hg(NO ₃) ₂	2	0.1060	0.1060	4	0
Pb(NO ₃) ₂	1/2	0.2120	0.2133	1	6
MnCl ₂	1/2	0.2120	0.2130	1	5
Co(NO ₃) ₂	1/2	0.2120	0.2135	0	7
Ni(NO ₃) ₂	1/2	0.2120	0.2132	1	6
Al(ClO ₄) ₃	1	0.1060	0.1060	0	0
La(ClO ₄) ₃	1/4	0.2120	0.2138	2	9
Ce(ClO ₄) ₃	1/4	0.2120	0.2131	2	5
Na ₃ AsO ₃	1/2	0.2120	0.2134	1	7
Na ₃ SbO ₃	1/2	0.2120	0.2475	100	168
Bi(NO ₃) ₃	1/2	0.2120	0.2126	2	3
Fe ₂ (SO ₄) ₃	1/2	0.2120	0.2858	1	348
CrCl ₃	1/2	0.2120	0.2132	1	6
Ti(SO ₄) ₂	1/4	0.2120	0.2664	10	304
Ti(SO ₄) ₂ *	1/4	0.1060	0.1516	200	430
ZrO(ClO ₄) ₂	1/4	0.2120	0.2609	1	231
SnCl ₄	1/2	0.2120	0.2911	8	373
VOCl ₂	1	0.1060	0.1070	4	5
UO ₂ (ClO ₄) ₄	1/2	0.2120	0.2241	100	57

*H₂O₂ was added before precipitation.

discernible conductimetric end point, when hydrogen ion ceases to be evolved from the reaction.

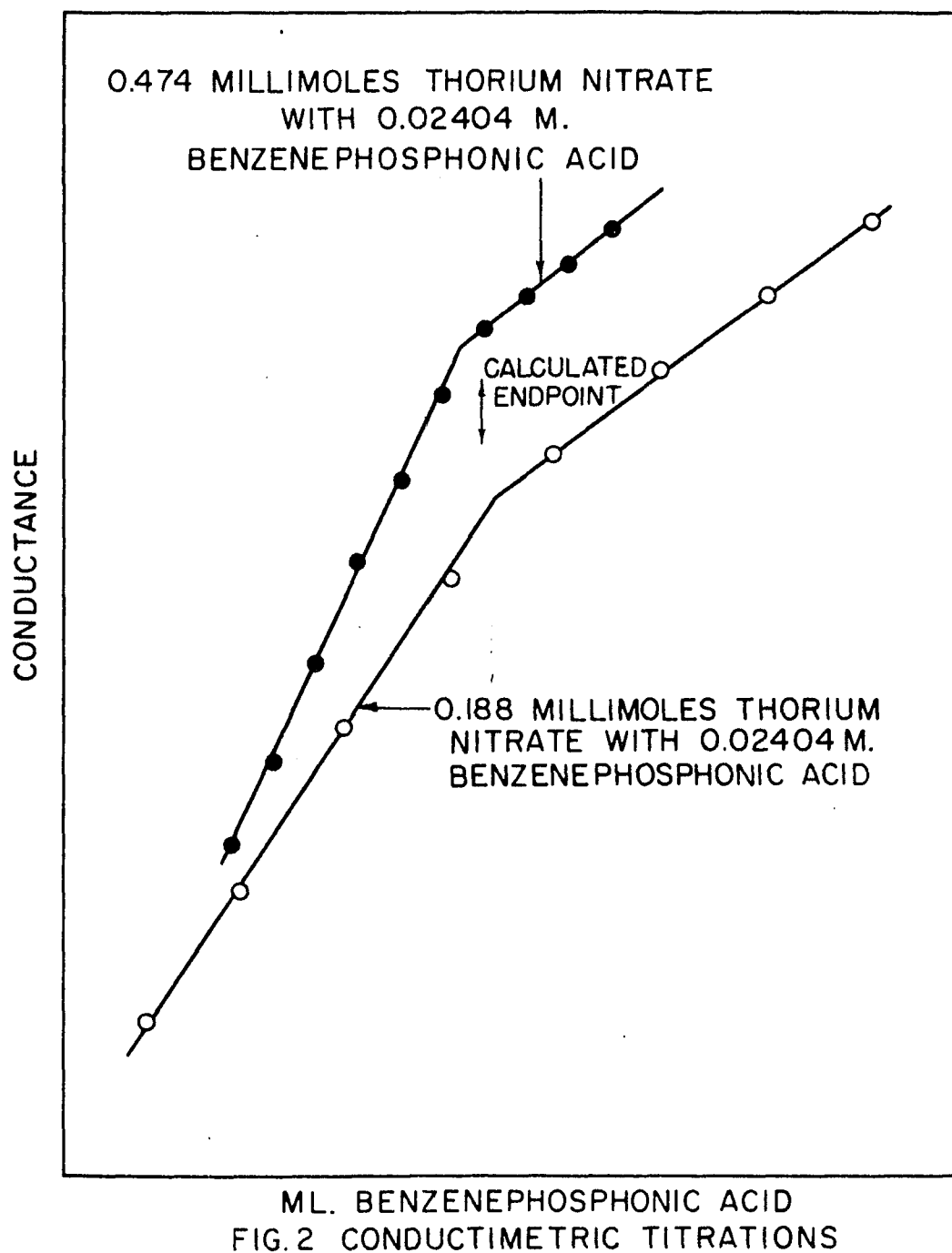
Titration were performed using 0.02404 M benzenephosphonic acid as titrant and portions of a 0.00959 M thorium nitrate solution in approximately 200 ml. of water, as samples. These titrations are shown in Fig. 2. The calculated end point is based on the equation above.

Titration of 0.5 millimolar thorium and less, showed very diffuse end points which appeared to occur much past the equivalence point.

b. Oscillometric. Titration of millimolar and 1/10 millimolar aqueous solutions of thorium nitrate with benzenephosphonic acid failed. Scale reading values were very high; near the end of the range, the changes in scale reading were small and the plots gently curved throughout the course of the titration.

In acetone, 1/10 millimolar solutions of thorium nitrate were titrated with some success. The end points were not admirably sharp and the end point error was of the order of a few per cent.

c. Adsorption indicator. A series of qualitative tests with a series of indicators in which a few drops of thorium solution were titrated with benzenephosphonic acid. Several indicators known to form colored thorium complexes were used; the remainder had been used as adsorption indicators (16). The following indicators were tested: thorin, carminic acid, chromazurol blue S, cacothelin, alizarin red S,



eriochrome black T, eosin, rhodamine 6G, metanil yellow, fluorescein, o-cresol phthalein, bromcresol purple, and bromphenol blue. Chromazurol blue S, carminic acid and eriochrome black T showed definite color changes but the end points were too diffuse to be of value.

Bromphenol blue was found to give a reasonably sharp end point in hot aqueous solution, 50 per cent alcohol or 25 per cent acetone. The color of this indicator is blue in water; the normal color at pH values greater than 4.6. Upon adding the thorium nitrate sample, the color changed to yellow, the normal acidic color. The first drop of benzenephosphonic acid changed the color to red, apparently due to adsorption on the suspension of thorium benzenephosphonate.

Another possible mechanism, that of complexation of thorium by the indicator, apparently does not occur here, since a titration of thorium with versene with bromphenol blue present does not show a color change in the vicinity of the equivalence point.

It was found that the reverse titration gave sharper end points. This was expected, since the indicating reaction in the reverse titration was adsorption of the anionic indicator. In the direct titration, desorption occurred at the end point.

A pH study showed that the greatest color difference between solutions before and after the equivalence point was observed at pH values between 3.0 and 4.5

Table 13 presents some typical results. Micro burets, 0.167 M benzenephosphonic acid and 0.0914 M thorium nitrate solutions were used. Fifteen drops of a 1 g. per 100-ml. bromphenol blue solution in alcohol were used as an indicator. The pH was kept between 3 and 4, and the first definite color change from yellow to pink was taken as the end point.

6. Solubility and solubility product of thorium benzenephosphonate 3-hydrate

The solubility of the thorium compound was determined spectrophotometrically in the pH range 0.48 to 1.96. Standard series of solutions of thorium benzenephosphonate were prepared at pH 0.5, 1.0 and 1.5 by diluting 0.000900 M benzenephosphonic acid with perchloric acid solutions of pH 0.5, 1.0 and 1.5, respectively. Appropriate volumes of 0.000457 M thorium nitrate were added last. The ionic strength of the perchloric acid solutions was previously adjusted to 1.0 by the addition of sodium perchlorate. The concentration range covered by the standard series was 1.80×10^{-6} to 9.00×10^{-6} M thorium benzenephosphonate.

Saturated solutions of thorium benzenephosphonate were prepared by two methods: 1) Excess thorium benzenephosphonate was shaken periodically with perchloric acid - sodium perchlorate solution of ionic strength one and varying pH from 0.48 to 1.96. 2) Excess thorium benzenephosphonate was heated to about 80° C. with acid perchlorate solutions of ionic strength one for about 8 hours, then

Table 13. Titrimetric Determination of Thorium with Benzenephosphonic Acid Using Bromphenol Blue As Adsorption Indicator

Mg. Th	
Taken	Found
6.0	5.8
15.8	15.5
19.8	19.4
23.5	23.3
27.6	27.1
35.0	34.9
39.0	38.8
43.0	42.6
46.9	46.5
50.3	50.4
54.0	54.3
58.3	58.2
67.8	67.8
77.2	77.5
96.8	96.9

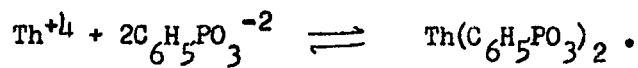
allowed to equilibrate for a week at room temperature. The room temperature involved in this experiment was controlled quite carefully, and was $25 \pm 2^\circ \text{C}$.

The spectra were observed with the Cary recording instrument in the range 250 to 290 $\text{m}\mu$. Ten-cm. matched silica cells were used. The peak at 263.0 $\text{m}\mu$ was measured. The precision in the absorbance measurements of the standard series of solutions at the three pH values used was not adequate to distinguish one set of data from the other two; therefore, one calibration curve was drawn from the data in Table 14. The curve drawn obeyed the equation

$$\text{Absorbance} = 0.625(\text{total analytical conc. of } \text{C}_6\text{H}_5\text{PO}_3\text{H}_2) + 0.14. \quad (5)$$

The absorbances and pH values observed in the various saturated solutions are also given in Table 14 along with the corresponding concentrations and calculated solubility products.

The solubility products were calculated with the assumption that the precipitating reaction is



The solubility product is then

$$K_{\text{SP}} = [\text{Th}^{+4}] [\text{C}_6\text{H}_5\text{PO}_3^{-2}]^2. \quad (6)$$

Benzenephosphonic acid is, however, only partially ionized at the pH values used in this work. The doubly charged anion concentration can be readily calculated from a knowledge of the ionization constants,

Table 14. Solubility and Solubility Product of
Thorium Benzenephosphonate 3-Hydrate

(b = 10.0 cm.; λ = 263.0 m μ)

Sample no.	pH	A	$M_{Th(C_6H_5PO_3)_2}$ $\times 10^{+6}$	$K_{SP} \times 10^{31}$
Calibration data				
1	0.50	1.30	9.00	
2	0.50	0.78	5.40	
3	0.50	0.56	3.60	
4	0.50	0.32	1.80	
5	1.00	1.32	9.00	
6	1.00	0.92	5.40	
7	1.00	0.80	3.60	
8	1.00	0.42	1.80	
9	1.50	1.10	9.00	
10	1.50	0.82	5.40	
11	1.50	0.62	3.60	
12	1.50	0.30	1.80	
Solubility data				
13*	0.48	1.54	1.07	5.41
14	0.52	1.40	0.96	5.38
15	0.52	1.40	0.96	5.38
16	0.96	0.45	0.24	2.12
17	0.99	0.35	0.16	0.77
18*	1.03	0.32	0.14	0.68
19	1.55	0.23	0.07	1.91
20	1.96	0.20	0.04	4.24
Av.				3.24

*Solutions prepared by method 2 which is described in text.

the analytical concentration of the acid and the pH.

$$[\text{C}_6\text{H}_5\text{PO}_3^-] = \frac{K_1 K_2 c_t}{K_1 K_2 + K_1 a_{\text{H}^+} + a_{\text{H}^+}^2}, \quad (7)$$

where c_t = Analytical concentration of the acid, or
in the solubility experiments, twice the
concentration of thorium benzenephosphonate, (8)

K_1 = First ionization constant of benzenephosphonic acid, (9)

K_2 = Second ionization of benzenephosphonic acid. (10)

The solubility products were then calculated from Equation 6. The thorium concentration was taken as the concentration of thorium benzenephosphonate corresponding to the absorbance observed. The benzenephosphonate concentration was calculated from Equation 7, using experimental values of c_t (twice the thorium benzenephosphonate concentration), and $[\text{H}^+]$ and ionization constants calculated potentiometrically in the next section ($K_1 = 0.91$, $K_2 = 6.41$). A summary of the findings are in Table 14.

7. Ionization constants of benzenephosphonic acid

The ionization constants of benzenephosphonic acid were determined from potentiometric titrations of about 4 millimoles of acid with 0.2444 N sodium hydroxide. Ionic strength was maintained at 1.0 continuously during the titrations by appropriate additions of a 4.0 M sodium perchlorate solution. Benzenephosphonic acid was recrystallized twice from deionized water for this work. The pH measurements were made with a Beckman Model G pH meter and a type 1190-90 Beckman glass electrode. The calculations of pK' values were made by classical means

(6) according to the following formula:

$$pK' = pH - \log(b + a_{H^+}) / (a - a_{H^+}), \quad (11)$$

where

$$a = \text{concentration of unneutralized acid, and} \quad (12)$$

$$b = \text{concentration of neutralized acid.} \quad (13)$$

In this calculation, the pH measurement observed with the pH meter was assumed to be equivalent to hydrogen ion activity; otherwise activity coefficients were ignored. The pK' values in Table 15 were results of several pH measurements from two titrations.

The ionization constants were also determined by an independent spectrophotometric method. Jaffe and Freedman (10) reported molar absorptivities for benzenephosphonic acid and the ionic species derived from this molecule. The values for the maxima of the secondary band in the ultraviolet were reported as follows: $C_6H_5PO_3H_2$, $\epsilon = 524$ at 263.5 m μ , $C_6H_5PO_3H^-$, $\epsilon = 383$ at 263.0 m μ and $C_6H_5PO_3^{2-}$, $\epsilon = 239$ at 258.0 m μ . This information showed that differences in molar absorptivities of the various species were large enough for a good determination of pK' values.

A series of 14 solutions of doubly recrystallized benzenephosphonic acid were prepared. Appropriate additions of sodium perchlorate, perchloric acid and sodium hydroxide were made in order to adjust the ionic strength to 1.0 and the pH to values distributed between zero and 10. The pH values were measured with a Beckman, Model G, pH meter, and

Table 15. The pK' Values of Benzenephosphonic Acid
by Potentiometric Titration

Titration 1		Titration 2	
pK'_1	pK'_2	pK'_1	pK'_2
0.92	6.51	0.80	6.33
0.99	6.51	0.89	6.29
0.86	6.50	0.93	6.29
0.93	6.51	0.96	6.31
0.97	6.50		6.34
Av. 0.93	6.51	0.89	6.31

Over-all av.:

$$pK'_1 = 0.91 \pm 0.02$$

$$pK'_2 = 6.41 \pm 0.10$$

the spectra observed by means of a Cary recording spectrophotometer. Absorbances were measured at 263.6 m μ . The analytical concentration, determined potentiometrically, of each solution was 0.002497 M in total benzenephosphonic acid. The pH values, absorbances and the quantities A/bc (where A is absorbance; b, length of the cell; and c, the concentration, i.e. the total benzenephosphonic acid concentration) of these solutions are tabulated in Table 16. A plot of these absorbance values vs. pH is included in Fig. 3. The pH value of ca. -0.3 in Table 16 and in Fig. 3 was estimated from the known quantity of perchloric acid used to prepare the solution.

The molar absorptivity of the dinegative anion $C_6H_5PO_3^{--}$ may be calculated directly from the absorbances measured at pH 8.16 and 9.61, since it is apparent from the curve (Fig. 3) that ionization was complete at these pH values and all of the benzenephosphonic acid was present as the dinegative anion. It has a value of 198 l./mole-cm.

Similarly, the molar absorptivity of the mononegative species, 394 l./mole-cm., was calculated from the absorbance observed at the midpoint of the break occurring at pH 2 to 4.5 (Fig. 3). The midpoint was determined graphically.

A knowledge of the molar absorptivities of the two ionic species made it possible to calculate the second ionization constant of benzenephosphonic acid according to the calculation below. The symbols used are defined as follows:

Table 16. Absorbance Values of Benzenephosphonic Acid
As a Function of pH

($b = 1.003$ cm.; $c = 0.002497$ M; $\lambda = 263.6$ m μ)

A	pH	A/bc
1.688	<u>ca.</u> -0.3	675
1.570	0.35	628
1.311	1.00	524
1.141	1.29	456
1.010	2.21	404
0.972	4.43	389
0.958	5.06	383
0.935	5.29	374
0.935	5.32	374
0.780	6.19	312
0.573	6.92	229
0.532	7.21	213
0.524	7.43	209
0.493	8.16	197
0.493	9.61	197

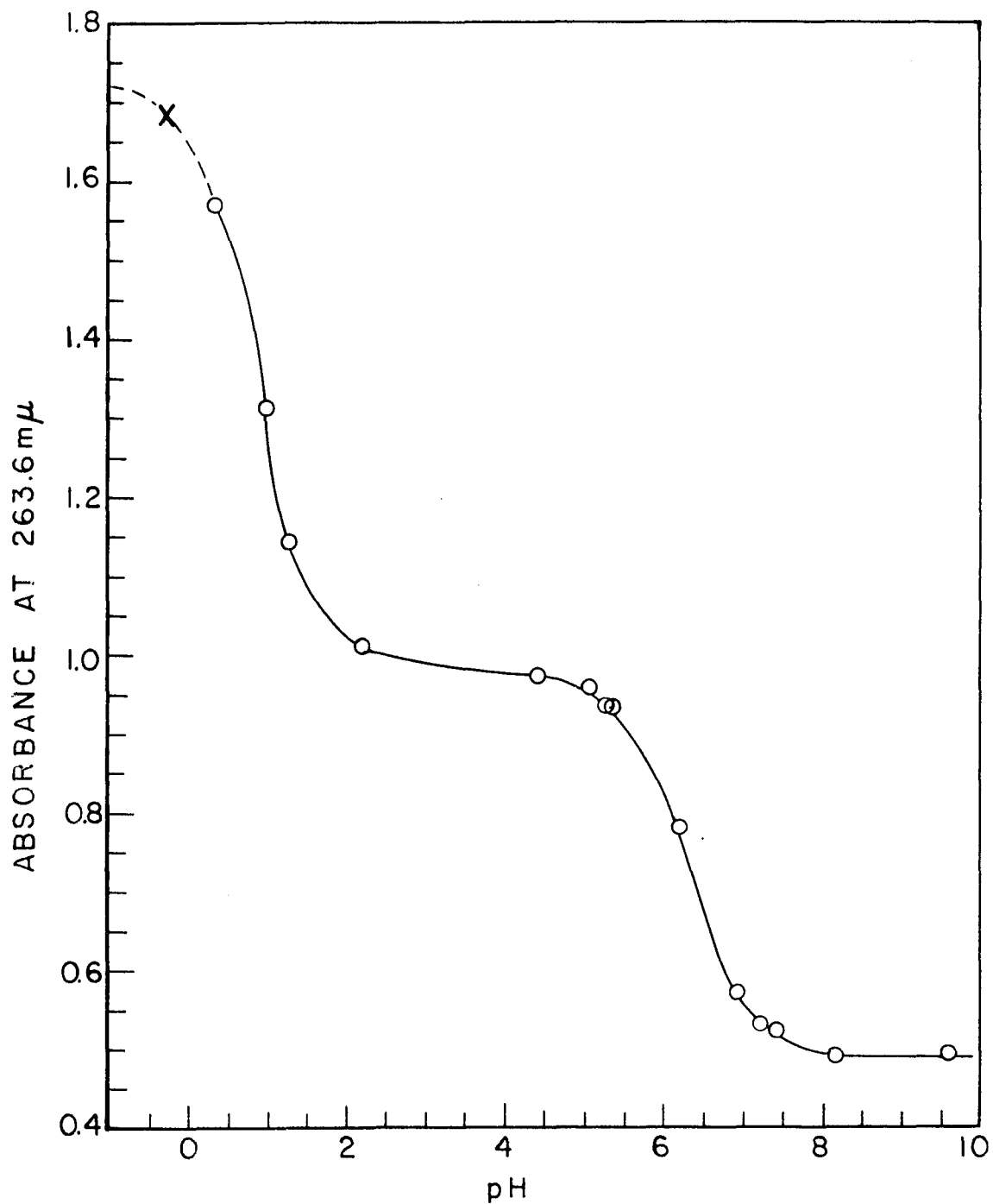


FIG. 3 ABSORBANCE VS. pH FOR BENZENEPHOSPHONIC ACID

$$K'_1 = \frac{a_{H^+} [C_6H_5PO_3H^-]}{[C_6H_5PO_3H_2]} \quad (14)$$

$$K'_2 = \frac{a_{H^+} [C_6H_5PO_3^{=}] }{[C_6H_5PO_3H^-]} \quad (15)$$

$$\epsilon_1 = \text{molar absorptivity of } C_6H_5PO_3H_2 \quad (16)$$

$$\epsilon_2 = \text{molar absorptivity of } C_6H_5PO_3H^- \quad (17)$$

$$\epsilon_3 = \text{molar absorptivity of } C_6H_5PO_3^{=} \quad (18)$$

$$c_t = \text{analytical concentration of benzenephosphonic acid} \quad (19)$$

$$A = \text{absorbance} \quad (20)$$

$$b = \text{length of cell.} \quad (21)$$

From Beer's law and the assumption that absorbances are additive,

$$A/b = \epsilon_1 [C_6H_5PO_3H_2] + \epsilon_2 [C_6H_5PO_3H^-] + \epsilon_3 [C_6H_5PO_3^{=}] \quad (22)$$

From the analytical concentration,

$$c_t = [C_6H_5PO_3H_2] + [C_6H_5PO_3H^-] + [C_6H_5PO_3^{=}] = 0.002494. \quad (23)$$

From the data in Fig. 3,

$$\epsilon_2 = 394 \text{ and} \quad (24)$$

$$\epsilon_3 = 197. \quad (25)$$

In the pH region 4 to 10, the concentration of the unionized species can be neglected and Equations 22 and 23 become

$$A/b = 394 [C_6H_5PO_3H^-] + 197 [C_6H_5PO_3^{=}] \text{ and} \quad (26)$$

$$0.002497 = [C_6H_5PO_3H^-] + [C_6H_5PO_3^{=}] \quad (27)$$

Equations 15, 26 and 27 may be combined to eliminate $[C_6H_5PO_3H^-]$ and $[C_6H_5PO_3=]$ and rearranged to the form

$$\frac{1}{0.986 - A/b} = \frac{a_{H^+}}{1.48 K'_2} + 0.678. \quad (28)$$

Equation 28 permits calculation of K'_2 from the slope of a plot of $1/(0.986 - A/b)$ vs. a_{H^+} . The pH values from 6.92 to 9.61 and corresponding absorbance values were plotted, according to Equation 28, and from the slope, K'_2 was calculated as follows:

$$\frac{\Delta a_{H^+}}{\Delta \frac{1}{0.986 - A/b}} = 1.48 K'_2, \quad (29)$$

$$K'_2 = 3.10 \times 10^{-7} \quad \text{and} \quad (30)$$

$$pK'_2 = 6.51. \quad (31)$$

The value of pK'_2 may also be taken directly from Fig. 3. From Equation 15 it can be seen directly that at the position where $[C_6H_5PO_3=]$ is equivalent to $[C_6H_5PO_3H^-]$, pK'_2 is equivalent to pH. This condition is met at the absorbance value half way between that of $C_6H_5PO_3H^-$ and that of $C_6H_5PO_3=$. At this absorbance the pH is 6.30. The previously calculated value is presumed to be the better value, since it was based on five measurements rather than primarily on one measurement, as in the latter case.

It was next desirable to obtain values for pK'_1 and ϵ_1 . It was not possible to obtain a value for ϵ_1 by the direct experimental method as was done for ϵ_2 and ϵ_3 , since at pH values less than zero, the ionic

strength value of one cannot be retained and, furthermore, at high acidities another species is apparently predominant. This postulated new species is evidenced by a very definite change in spectra. It was possible to determine values for pK'_1 and ϵ_1 which were consistent with each other and also consistent with the absorbance-pH data available.

In the pH region of interest here, $[C_6H_5PO_3^-]$ can be neglected and the following are true. From Equations 22 and 24,

$$A/b = \epsilon_1 [C_6H_5PO_3H_2] + 394 [C_6H_5PO_3H^-] \quad (32)$$

From Equation 23,

$$0.002497 = [C_6H_5PO_3H_2] + [C_6H_5PO_3H^-] \quad (33)$$

A combination of Equations 14, 32 and 33 designed to eliminate $[C_6H_5PO_3H_2]$ and $[C_6H_5PO_3H^-]$ can yield the following equation:

$$a_{H^+} = K'_1 c_t (\epsilon_1 - \epsilon_2) \frac{1}{c_t \epsilon_1 - A/b} - K'_1 \quad (34)$$

A series of estimated values of ϵ_1 in the neighborhood of that predicted by the potentiometrically observed value of K'_1 were inserted in Equation 34. Corresponding to each insertion, a plot of $1/(c_t \epsilon_1 - A/b)$ vs. a_{H^+} was prepared, the best straight line drawn and a value of K'_1 from the intercept on the a_{H^+} axis was taken. At the position where $1/(c_t \epsilon_1 - A/b)$ is zero,

$$a_{H^+} = -K'_1 \quad (35)$$

At the position where the absorbance was equal to $(\epsilon_1 b c_1 - \epsilon_2 b c_2)/2$,

it was known that $[\text{C}_6\text{H}_5\text{PO}_3\text{H}_2]$ is equivalent to $[\text{C}_6\text{H}_5\text{PO}_3\text{H}^-]$; and from Equation 14,

$$\text{pK}'_1 = \text{pH}. \quad (36)$$

Values for pK'_1 were taken from a plot similar to Fig. 3 and compared to the pK'_1 values obtained graphically as explained above. A comparison of these values is given in Table 17. As is shown in the table, the best agreement occurs when ϵ_1 is given the value of 690 l./mole-cm., which gives pK'_1 a value of 0.96.

8. Absorption spectra of benzenephosphonic acid and derived ionic species

The ultraviolet absorption spectra in the range 250 to 290 m μ of benzenephosphonic acid in perchlorate solution of ionic strength one at pH values of 9.61 and 8.16, previously discussed in reference to the spectrophotometric determination of pK' values, gave directly the absorption spectrum of $\text{C}_6\text{H}_5\text{PO}_3^-$. The proof of the purity of this species was shown in Fig. 3. The concentration of the solution used was 0.002497 M. The spectra are shown in Fig. 4 and molar absorptivities at absorption maxima are tabulated in Table 18.

The spectrum of benzenephosphonic acid at pH 4.43, also used in the pK' determinations, was used to determine the spectrum of $\text{C}_6\text{H}_5\text{PO}_3\text{H}^-$. At this pH, $[\text{C}_6\text{H}_5\text{PO}_3\text{H}_2]$ can be neglected and Equation 21 takes the following form:

$$A/b = \epsilon_2 [\text{C}_6\text{H}_5\text{PO}_3\text{H}^-] + \epsilon_3 [\text{C}_6\text{H}_5\text{PO}_3^-]. \quad (37)$$

Table 17. Calculated pK'_1 Values for
Estimated ϵ_1 Values

Estimated ϵ_1	pK'_1 from intercept	pK'_1 from A vs. a_{H^+}
695	0.89	0.96
690	0.96	0.96
685	1.03	0.97
680	1.08	0.97
675	1.15	0.97
670	1.24	0.97

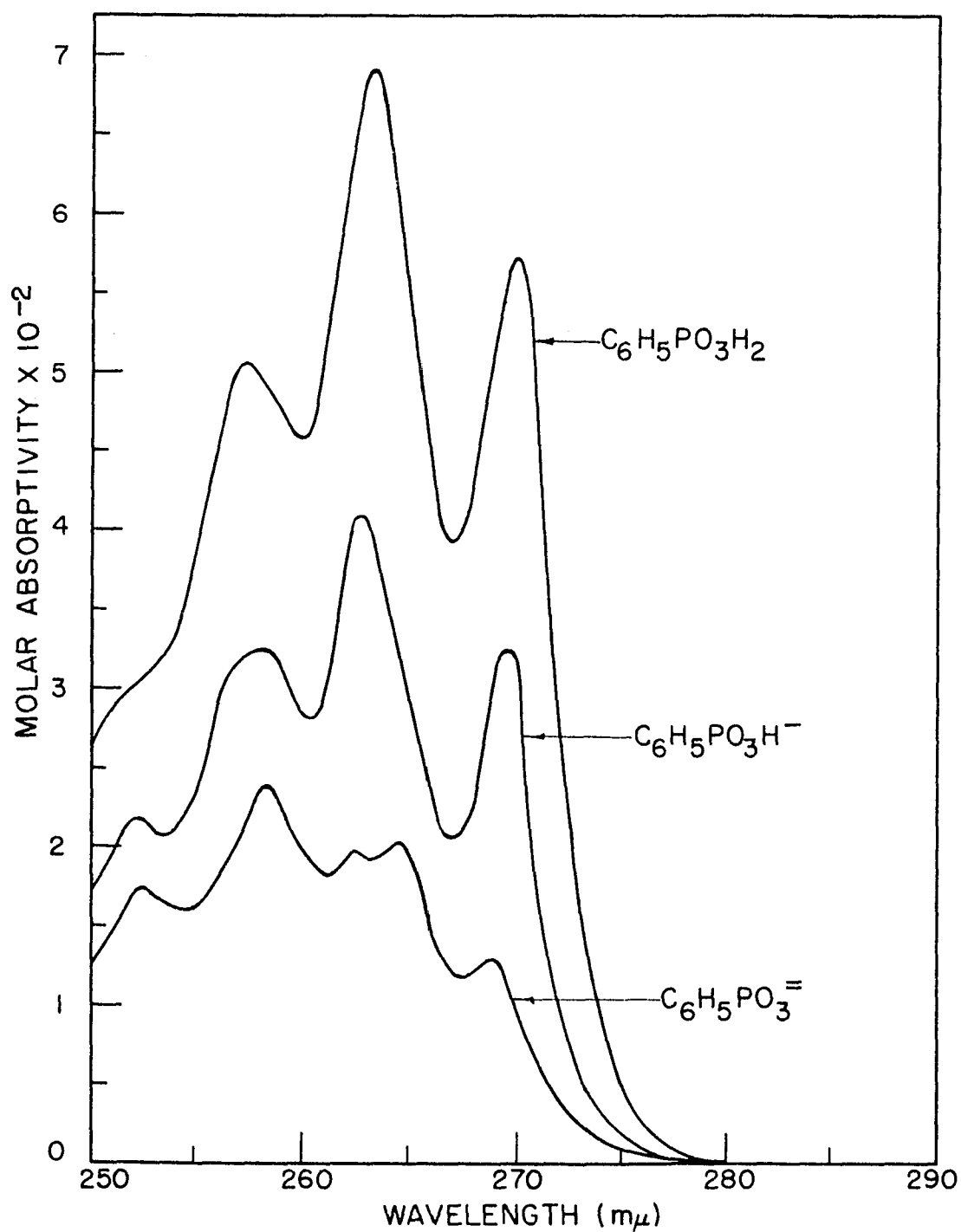


FIG.4 ABSORPTION SPECTRA

Table 18. Absorption Spectral Data for Benzenephosphonic
Acid and Derived Ionic Species

(Range investigated: 250 - 290 m μ)

$\text{C}_6\text{H}_5\text{PO}_3^-$		$\text{C}_6\text{H}_5\text{PO}_3\text{H}^-$		$\text{C}_6\text{H}_5\text{PO}_3\text{H}_2$		$(\text{C}_6\text{H}_5\text{PO}_3\text{H}_3^+)$	
$\lambda(\text{m}\mu)$	ϵ_{max}	$\lambda(\text{m}\mu)$	ϵ_{max}	$\lambda(\text{m}\mu)$	ϵ_{max}	$\lambda(\text{m}\mu)$	ϵ_{max}
252.4	174	252.2	218				
258.4	242	258.1	325	257.3	505	260.3	938
262.5	197	262.7	416	263.6	690	265.5	1288
264.6	202						
268.8	129	269.6	325	270.1	573	272.4	1059

The absorbance, length of the cell, and ϵ_3 are known directly. From the total concentration (0.002497 M) and the relative concentrations of $C_6H_5PO_3H^-$ and $C_6H_5PO_3=$, the concentration terms can be evaluated. The relative concentration was determined from Fig. 3 according to the following manipulation. At any point on Fig. 3, in this case the point at pH 4.43, let

$$A_x = \text{absorbance observed.} \quad (38)$$

Then, from Beer's law and the assumption that absorbances are additive,

$$A/b = \epsilon_2 [C_6H_5PO_3H^-] + \epsilon_3 [C_6H_5PO_3=] . \quad (39)$$

It also follows from the definition of c_t , Equation 23 that

$$A_x/b = (\epsilon_2 - \epsilon_3) [C_6H_5PO_3H^-] + \epsilon_3 c_t . \quad (40)$$

Solving for $[C_6H_5PO_3H^-]$,

$$[C_6H_5PO_3H^-] = \frac{(A/b - \epsilon_3) c_t}{\epsilon_2 - \epsilon_3} . \quad (41)$$

From Equation 41 and the data in Fig. 3, it was found that at pH 4.43

$$[C_6H_5PO_3H^-] = 0.987 c_t . \quad (42)$$

These data, corresponding to several wavelengths, were fed into Equation 39 and ϵ_2 values were calculated. In this way the spectrum of 97.8 per cent $C_6H_5PO_3H^-$ and 2.2 per cent $C_6H_5PO_3=$ was corrected to 100 per cent $C_6H_5PO_3H^-$. Since the wavelength shift at the peaks in the spectra at pH 2.21 and 4.43 was insignificant, no wavelength correction was necessary. The data discussed are found in Fig. 4 and in Table 18.

In a strictly analogous fashion the spectra observed in pK' study, at pH ca. -0.3 were corrected for the $C_6H_5PO_3H^-$ present, to obtain the spectrum of $C_6H_5PO_3H_2$. In this case $[C_6H_5PO_3^-]$ was neglected and

$$A_y/b = \epsilon_1 [C_6H_5PO_3H_2] + \epsilon_2 [C_6H_5PO_3H^-] . \quad (43)$$

From Fig. 3, in a manner similar to the previous calculation, it was found that

$$[C_6H_5PO_3H_2] = 0.952 c_t . \quad (44)$$

In the case of $C_6H_5PO_3H_2$, wavelength shifts of maxima due to the contaminating species were considered to be insignificant in light of the close similarity of the position of maxima in the two species. The spectral data for $C_6H_5PO_3H_2$ are also included in Fig. 3 and Table 18. As in the previous cases the wavelength range observed was from 250 to 290 $m\mu$.

In the course of the pK' determinations the spectrum of benzenephosphonic acid (0.002497 M) from 250 to 290 $m\mu$, in concentrated perchloric acid was observed. A spectrum significantly different from that of $C_6H_5PO_3H_2$ was found. It was postulated that in the highly acidic media, a new specie was formed by the addition of a proton to the benzenephosphonic acid molecule. The data observed were recorded in Table 18.

IV. DISCUSSION

A. The Compounds of Thorium with
Benzenephosphonic Acid and Derivatives1. The compounds of thorium with benzenephosphonic acid

Thorium forms a white insoluble compound with benzenephosphonic acid. Conductimetric, oscillometric and adsorption indicator titrations showed end points corresponding to a thorium to benzenephosphonate ratio of 1:2. This was exactly the stoichiometry expected in order that the charge requirements be satisfied.

Even after ignition of this compound at 1200° C. no phosphorus is lost, as is shown by the retainment of the 1:2 ratio of thorium to phosphorus which was calculated from the phosphate analysis (Table 9) of the material ignited at 1200° C.

$$\text{Th/P} = \frac{(\text{wt. ppt. } 120^\circ \text{ C.})(\% \text{ Th in ppt. } 120^\circ \text{ C.})(30.98)}{(\text{wt. ppt. } 1200^\circ \text{ C.})(\% \text{ P in ppt. } 1200^\circ \text{ C.})(232.12)} \quad (45)$$

$$= 0.500 \quad (46)$$

$$= 0.499 \quad (47)$$

$$= 0.499 \quad (48)$$

Since the thorium to phosphorus ratio was 1:2 at the beginning and end of the series of ignition products, it must have remained so through the entire course of the ignition. This calculation assumes only that no thorium is lost upon ignition.

Each of the series of compounds observed upon ignition will be discussed in turn. The analysis of the dried (150° C.) material was 38.76 ± 0.14 per cent thorium (Tables 7 and 11) and 52.4 ± 0.2 per cent $\text{C}_6\text{H}_5\text{PO}_3$ (Table 10). These results agree well with 38.79 per cent thorium and 52.18 per cent $\text{C}_6\text{H}_5\text{PO}_3$ calculated for $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$. Consideration of the precision of the analytical results definitely established the compound as the trihydrate rather than any other compound considered in Table 19.

The upper limit of thermal stability of this compound was established as 180° to 190° C. by the drying temperature study (Table 3.). This limit agrees reasonably well with the 210° to 250° C. observed in the thermogravimetric curves (Table 6 and Fig. 1).

The next stable compound was observed in the temperature range from 250° to about 450° C. (Tables 6 and 7 and Fig. 1). The thorium analysis (Table 7) of 39.96 ± 0.29 per cent agreed very well with 40.00 per cent thorium for $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$. The manifestation of this compound was expected inasmuch as the eight oxygen atoms available conveniently fill the coordination sphere of the central thorium atom. The structure below is suggested as that of $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$.

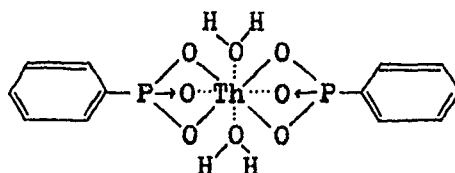
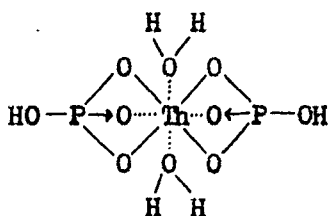


Table 19. Comparison of Observed and Calculated
Analyses of the Compounds Observed on
Ignition of Thorium Benzenephosphonate 3-Hydrate

Compound	Molecular wt.	% Th	% $\text{C}_6\text{H}_5\text{PO}_3$	% P
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 4\text{H}_2\text{O}$	616.3	37.66	50.66	
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3.5\text{H}_2\text{O}$	607.3	38.22	51.41	
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$	598.3	38.79	52.18	
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 2.5\text{H}_2\text{O}$	589.3	39.39	52.98	
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$	580.3	40.00	53.80	
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot \text{H}_2\text{O}$	562.3	41.28		
$\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2$	544.3	42.65		
$\text{Th}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$	460.1	50.45		
$\text{Th}(\text{HPO}_4)_2$	424.1	54.73		14.61
ThP_2O_7	406.1	57.16		15.26
ThO_2	264.1	87.89		0.00
Sample dried 150° C.		38.76	52.4	
Sample dried 250° C.		39.96		
Sample ignited 500° C.		50.12		
Sample ignited 1200° C.		54.65		14.6

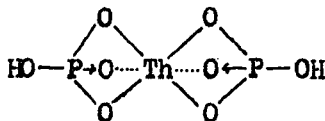
A stable compound was observed in the temperature range from 500° to about 800° C. (Tables 6 and 7 and Fig. 1). The thorium analysis from ignition studies (Table 7) gave 50.12 ± 0.36 per cent thorium. The analysis agrees well with the 50.45 per cent thorium calculated for $\text{Th}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$. The suggested structure below retains the coordination number of eight for thorium.



Some of the findings of Duval (5) tend to substantiate the feasibility of retaining water of constitution at temperatures in the range of 800° C. Thorium pyrophosphate retains water to 540° C.; thorium hydroxide starts to decompose at 380° C., but the transition to the oxide is not complete until a temperature of 747° C. is reached. The ignition of the thorium-8-quinolinolo- complex was carried out up to 945° C., at which temperature rapid weight loss was still occurring.

The final compound in the series, stable from 900 to 1200° C. (Tables 6 and 7 and Fig. 1) gave thorium analyses of 54.36, 54.40 and 54.65 per cent thorium ignited to 900°, 1000° and 1200° C., respectively. These results agree very well with the 54.73 per cent thorium calculated for $\text{Th}(\text{HPO}_4)_2$. Phosphorus analyses (14.6 per cent observed as compared to 14.6 per cent calculated) also agree with the afore-mentioned formula.

Below is a suggested structural formula.



Duval (5) reported three cases showing unusual tenacity of phosphates for the elements of water, which tend to substantiate the present findings. Boron phosphate is converted to the pyrophosphate very slowly at 946° to 1000° C. Chromium phosphate continuously loses water up to 946° C. $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ is converted to ZrP_2O_7 only after heating to 850° to 880° C.

Duval (5) studied the ignition of titanium p-hydroxybenzenearsonate and five organic arsonates of zirconium, including the benzenearsonate. In each case the ignition proceeds to the oxide. The ignitions are all complex, as indicated by the number of inflections in the pyrolysis curves, but there are no plateaus sufficiently flat to allow any distinction of intermediate compounds. Duval has not studied the ignition of any thorium organic arsonates. Welcher (37) stated that the thorium precipitate of benzenearsonic acid has the composition $\text{Th}(\text{C}_6\text{H}_5\text{AsO}_3)_2$. The original papers quoted by Welcher (8, 12, 13, 32, 39) do not establish this composition. It has been found that ignition of thorium benzenearsonate does not drive off arsenic quantitatively (32).

2. The compounds of thorium with phosphobenzene

The pyrolysis curves (Table 6 and Fig. 1) of the precipitate formed with phosphobenzene presented the same plateaus at roughly the same

temperatures, indicating that identical compounds are formed. This is consistent with the idea that phosphobenzene hydrolyzes to benzenephosphonic acid before reaction with thorium.

3. The reaction of thorium with dimethylbenzenephosphonate

Few conclusions may be drawn, as the information obtained about this reaction is insufficient. The pyrolysis curves (Table 6 and Fig. 1) showed conclusively that the same series of compounds as observed with benzenephosphonic acid were not manifested with the dimethyl ester. It logically follows that the reaction with thorium did not occur after the complete hydrolysis of the ester. It was also observed that the reaction occurred slowly, which is consistent with a suggestion that the reaction probably occurs with the half hydrolyzed ester. Some semi-quantitative tests indicated that the molecular weight of the initial product was of the order of 900, which would allow the possibility of a reaction of thorium with four molecules of reagent. The two pyrolysis curves (Table 6) given for the thorium compound formed with dimethylbenzenephosphonate do not agree very well, which indicates the easily conceived possibility of a non-homogeneous precipitate. The pyrolysis data are not precise enough for one to be sure of this.

B. Analytical Usage of Benzenephosphonic Acid and Derivatives

1. Gravimetric

Quantitative precipitation of thorium with benzenephosphonic acid as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$ was effected from pH 0.5 to 3.5 (Table 4) but not

at 0.1 pH. A pH of 0.5 to 1.0 was chosen for precipitation in the recommended procedure, because the low pH range was expected to eliminate the effect of likely interfering ions. At pH 0.5 a four-fold or greater excess of reagent was found necessary for quantitative precipitation (Table 5). A five-fold excess was recommended in the procedure to allow a reasonable safety factor. The bulk of the precipitation was best carried out in about 4 N hydrochloric acid to insure precipitation of a filterable material. At best, the precipitate was not notably easy to handle. Some of the precipitate was always contained in a foam on top of the solution, and this portion of the precipitate showed a tendency to creep. This property is not thought to have contributed to the error observed, however. It was also observed that the precipitate adhered tenaciously to scratches on the surface of the glass precipitation vessel.

The thermogravimetric curves of $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$ displayed four plateaus corresponding to $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{Th}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Th}(\text{HPO}_4)_2$. The last plateau, corresponding to $\text{Th}(\text{HPO}_4)_2$, is of no practical analytical use. First, because it appears above the temperature range at which filter crucibles can be used (900°C.) and, in fact, above the practical range for continuous operation of resistance furnaces (900° to 1000°C.). Second, because ignition even at 1200°C. was very slow, requiring 8 hours or more before constant weight was achieved. This is probably due to a slow evolution of the last traces of carbon, as is observed in the ignition of MgNH_4PO_4 with filter paper (40).

Ignition to $\text{Th}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ is not advisable on the basis of the fairly large slope (2 mg. per 100°C.) of the plateau in the pyrolysis curve corresponding to this compound. Furthermore, $\text{Th}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$, prepared by ignition of $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$ retains an objectionable amount of carbon up to its decomposition temperature. This is evidenced by the grey color of the precipitate and the low thorium content observed (50.12 per cent thorium compared to 50.45 per cent thorium calculated).

Ignition to $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 2\text{H}_2\text{O}$ as a weighing form is feasible, but the trihydrate was chosen in preference because the observed precision was slightly better.

The proper drying temperature was determined by the experiment summarized in Table 3. Although this experiment involved changes in pH of precipitation and sample size since there is no trend related to either of these functions, all these data were considered significant to the problem of determining drying temperature. The proper drying temperature range was taken as 140° to 180°C. for thorium benzene-phosphonate 3-hydrate. In this range are found five out of 20 results with a weight change of greater than 0.0003 g., i.e. greater than the probable error involved in a difference of two weights made on an analytical balance. The largest weight change was 0.0006 g. corresponding to two parts per thousand change relative to the precipitate weight. The average change in the temperature range 140° to 180°C. was 0.24 mg., or about one part per thousand.

The analyses (Table 11) show an average deviation in 22 results of 3.7 parts per thousand from the theoretical, or on the average an absolute error of ± 0.1 mg. of thorium. The apparent constant error is much smaller than the precision, so a constant error in this method cannot be assumed.

The interference study showed a general small positive interference, up to 1 per cent, from nearly all the cations tested (Table 12). This appears to indicate a general difficulty due to adsorption of foreign cations, even though the general precipitating procedure for obtaining pure precipitates suggested by Kolthoff (15) was used. That is, the precipitation was made from concentrated solution; the suspension was diluted with water and digested overnight before filtration. Probably digestion in fairly concentrated (1 N) hydrochloric acid overnight on a hot plate would improve the results. Certain of the bad positive interferences were expected, including the tetravalent ions of titanium, zirconium and tin. Positive interference from trivalent iron and antimony also was not surprising in view of the information available about the use of organic arsonic acid reagents. Interference from uranium, silver and thallium were also observed. In the cases of the latter two, it should be mentioned that nitric acid was used in place of hydrochloric acid which was recommended in the general procedure.

Certain potential interferences which were not observed are notable, including Ce(III), La(III) and Bi(III).

A multitude of gravimetric separations and determinations of thorium have been used (34). The classical oxalate precipitation probably remains the most generally applicable with the rare earth ions as the only serious interferences. Large amounts of several cations interfere (34) to some extent, including Ca(II), Sr(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II), Sn(II), Pb(II) and Bi(III). Zr(IV), U(VI) and Fe(III) remain in solution by virtue of complex formation. The determination is readily completed by ignition to the oxide.

Precipitation as the iodate (34, 4) has been used classically to supplement the oxalate method, in that the iodate precipitation separates thorium from the rare earth ions. Drying and weighing of $4\text{Th}(\text{IO}_3)_4 \cdot \text{KIO}_3 \cdot 18\text{H}_2\text{O}$ at 40° to 45° C. has been recommended (4) and contested (5, 29). The determination is usually completed volumetrically (29) or by means of a second precipitation with oxalate.

The pyrophosphate method separates thorium from the rare earth ions, although several precipitations are sometimes necessary (34).

The rare earths are apparently coprecipitated with thorium in the benzenearsonic acid precipitations (34). The determination must be completed by an oxalate precipitation (32).

The gravimetric method proposed in this paper offers a way of separating thorium by means of one precipitation in the presence of small amounts of Ce(III), La(III) and Bi(III). Interference from small amounts of other rare earth ions can reasonably be assumed not to exist,

so this method offers an optional means of supplementing the oxalate method for thorium. It would have an advantage over the iodate method in that the determination could be completed in one step. The high molecular weight of the precipitate gives another advantage to the proposed method.

2. Titrimetric

Conductimetric and oscillometric detection of the end point cannot be recommended for analytical use.

The adsorption indicator method cannot be strongly recommended on the basis of the data available. It was found that the end point became difficult to see if the sample was much larger than 0.1 g. of thorium. It was also observed that end points were very diffuse if the titrations were carried out in acetate buffer solutions, probably due to increased ionic strength.

C. Physical Constants Determined

1. Solubility and solubility product of thorium benzenephosphonate 3-hydrate

The solubility data are not highly precise, since in the determination very low absorbances were observed with 10-cm. cells. The agreement in the calculated solubility products (Table 14), although not startling, is quite good considering that any error in observed concentration is cubed in the solubility product. Ionic strength was maintained at 1.0 in this work with sodium perchlorate and perchloric acid.

It is interesting to calculate the error in the gravimetric method from solubility. At pH zero, i.e. just outside the range of quantitative precipitation (Table 4), the solubility error would be approximately 0.2 mg.

2. Ionization constants of benzenephosphonic acid

The values obtained by this worker did not agree well with previously reported values. Table 20 compares the reported values with the ones found in this work.

The works of Jaffe' (11) and Lesfaurier (22) were both done potentiometrically; neither work was done at constant ionic strength. The values from the present work are considered by the author to be better values inasmuch as the ionic strength was maintained at 1.0 and results from two independent experimental methods were used and found to check each other reasonably well.

No effort was made to estimate activity coefficients; therefore, these results are concentration equilibrium constants rather than thermodynamic constants.

Table 20. Comparison of pK' Values Observed
in This Work with Those Previously Reported

	Jaffe' et al. (11)	Lesfaurier et al. (22)	This work potentio- metric	This work spectropho- tometric
pK'_1	1.83	1.60	0.91	0.96
pK'_2	7.07	6.85	6.41	6.51

3. Absorption spectra of benzenephosphonic acid and derived ionic species

The wavelengths at maximum absorption agree very well with the work of Jaffe' (10), but the molar absorptivities do not, as shown in Table 21. A portion of the discrepancy can be ascribed to the difference in pK' values in the two works (11).

Table 21. Comparison of Molar Absorptivities and Wavelengths of Maximum Absorption Observed in This Work with Those Previously Reported

	$C_6H_5PO_3^-$		$C_6H_5PO_3H^-$		$C_6H_5PO_3H_2$	
	$\lambda(m\mu)$	ϵ_{max}	$\lambda(m\mu)$	ϵ_{max}	$\lambda(m\mu)$	ϵ_{max}
Jaffe' (10)	258.0	239	263.0	383	263.5	524
This work	258.4	248	262.8	403	263.4	690

The $C_6H_5PO_3H_3^+$ species suggested to account for the spectra observed in concentrated perchloric acid cannot be discussed very fully as too little is known about it. It seems reasonable to expect this specie to form, however, in the very acid media (23), even as similar species form with carboxylic acids (1).

D. Suggestions for Further Work

It is suggested that the following investigations be made to further the work reported in this thesis.

1) The gravimetric method discussed in this paper should be tested for interference by rare earth ions other than the two already tested. Varying amounts of interfering rare earth ions should be tried.

2) A methodical study of wash solutions might find a method of alleviating the small positive interferences observed with most cations.

3) The dimethyl ester of benzenephosphonic acid was found to homogeneously precipitate thorium quantitatively in an extremely easily filtered form. This problem would be interesting to pursue, although one would first want to prove homogeneity of the precipitate before proceeding to any great length with the work. A few pyrolysis curves on precipitates formed under somewhat different conditions should prove homogeneity or non-homogeneity.

4) More study should be expended on the suggested titrimetric method for thorium involving an adsorption indicator. A methodical interference study should prove the merit of the method.

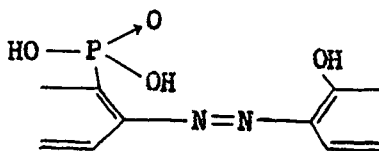
5) This work was limited to a study of benzenephosphonic acid with thorium. It is known that the compounds formed by titanium and zirconium with benzenephosphonic acid are also only slightly soluble. It would be of interest to ascertain the analytical importance of these compounds. Here, too, pyrolysis curves would supply a large share of the information desired.

6) The most obvious extension of this work would lie among the different phosphonic acid reagents. Substituted benzenephosphonic acids

probably would not be significantly different from the unsubstituted compound. Substituted benzenearsonic acids have not shown properties very significantly different from those of the parent compound (11, 14, 37). Jaffe et al. (11) pointed out that since the Hammett (9) reaction constant for the ionization of the benzenephosphonic acids is less than that for the benzenearsonic acids (31), less effect by substituents can be expected in the case of the benzenephosphonic acids. The author hesitates to recommend work in this direction.

7) This work has included the attempted use of a few hydrolyzable derivatives of benzenephosphonic acid. More derivatives could be tried, but the work done with the methyl ester indicates that thorium reacts with the half hydrolyzed material, and the probability of obtaining a homogeneous precipitate under these conditions is not very good.

8) It would be interesting to compare o-hydroxyazo compounds having a phosphono group in the ortho position with the analogous arsenic compounds studied originally by Kusnetsov (20, 21).



9) It would be interesting to learn more about the postulated cationic species observed spectrophotometrically in highly acid solutions of benzenephosphonic acid.

V. CONCLUSIONS

- 1) Thorium is precipitated by benzenephosphonic acid as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$. Upon ignition the trihydrate loses a molecule of water forming a dihydrate, which is stable from 250° to about 450° C. From 500° to about 800° C., the occurrence of $\text{Th}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ is indicated. From 900° to 1200° C. $\text{Th}(\text{HPO}_4)_2$ was found.
- 2) Phosphobenzene, an anhydro compound of benzenephosphonic acid, also precipitates thorium as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$.
- 3) Dimethylbenzenephosphonate precipitates thorium, apparently in an homogeneous fashion, but not as $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$. It is indicated that the reaction uses four moles of the ester per mole of thorium. The product is suspected to be non-homogeneous.
- 4) A gravimetric method for thorium is proposed, in which thorium is precipitated with a five-fold excess of benzenephosphonic acid at a pH greater than 0.5, preferably 0.5 to 1.0. The analysis is completed by filtering, washing with 1 M hydrochloric acid and drying at 150° C. to $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$.
- 5) Adsorption apparently gives rise to a positive error up to 1 per cent for many foreign cations. The serious interferences were from Ti(IV), Zr(IV), Sn(IV), U(VI), Fe(III), Sb(III), Ag(I) and Tl(I). Notable separations were made from small amounts of Ce(III), La(III), Bi(III) and Al(III).

6) The method is offered as a supplementary method to the classical oxalate procedure, since it separates thorium from small amounts of rare earth ions. It would have an advantage over the iodate method usually employed for this separation, in that the analysis can be made without a second precipitation.

7) A titrimetric method using bromphenol blue as an adsorption indicator has been shown to function adequately on pure thorium nitrate solutions.

8) The solubility of thorium benzenephosphonate was determined in the pH range 0.48 to 1.96. The solubility product ($K_{SP} = [Th^{+4}] [C_6H_5PO_3^{=}]^2$) was found to be of the order of 3.24×10^{-31} .

9) The pK' values were determined potentiometrically and spectrophotometrically. The pK'_1 values 0.91 and 0.96 and pK'_2 values 6.41 and 6.51 for the potentiometric and spectrophotometric determinations, respectively, agree reasonably well.

10) Absorption spectra of the species $C_6H_5PO_3^{=}$, $C_6H_5PO_3H^{-}$, and $C_6H_5PO_3H_2$ were determined in the range 250 to 290 m μ . The agreement with the literature data available is reasonably good (9). Isolation of each species was insured by corrections based on a pH vs. absorbance plot. Data from the spectra of a proposed $C_6H_5PO_3H_3^{+}$ specie are reported.

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VII. ADDENDA

A. Rare Earth Interference

A significant experiment concerning rare earth interference in the gravimetric method proposed was performed after the thesis was written, the data of which are presented in Table 22. It was shown that small amounts of lanthanum or cerium do not interfere, and it was desired to know if larger amounts would be bothersome.

Table 22. A Study of Rare Earth Interference

Interfering substance	Amount interfering cation (g.)	Wt. Th taken	Wt. Th found	No. of results	Error (mg.)
La(ClO ₄) ₃	0.025	0.2120	0.2138	2	1.8
Ce(ClO ₄) ₃	0.025	0.2120	0.2131	2	1.1
Ce(NO ₃) ₃	0.025	0.1060	0.1075	3	1.5
Ce(NO ₃) ₃	0.050	0.1060	0.1069	3	0.9
Ce(NO ₃) ₃	0.100	0.1060	0.1088	3	2.8
Ce(NO ₃) ₃	0.150	0.1060	0.1114	3	5.4
Ce(NO ₃) ₃	0.200	0.1060	0.1119	3	5.9
Ce(NO ₃) ₃	0.250	0.1060	0.1197	3	13.7
Mixture of	0.105	0.1060	0.1189	1	12.9
Ce, La, Sm, Pr,	0.210	0.1060	0.1244	1	18.4
Nd, Er, Yb	0.315	0.1060	0.1666	1	60.6
*Ce(NO ₃) ₃	0.200	0.1060	0.1072	2	1.2
*None		0.1060	0.1052	1	- 0.8
**Ce(NO ₃) ₃	0.200	0.1060	0.1078	2	1.8
**None		0.1060	0.1056	1	- 0.4
***Ce(NO ₃) ₃	0.200	0.1060	0.1065	1	0.5

* One gram citric acid added prior to precipitation.

** Fe(III) Specific Versene, 0.5 ml. added prior to precipitation.

*** Precipitation made in twice the recommended volume of solution.

The data show that rare earth ions do indeed interfere. Use of citric acid or Fe(III) Specific Versene (Bersworth Chemical Company, Framingham, Massachusetts) to complex the rare earth ion cannot be recommended since thorium precipitation is apparently retarded as well.

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